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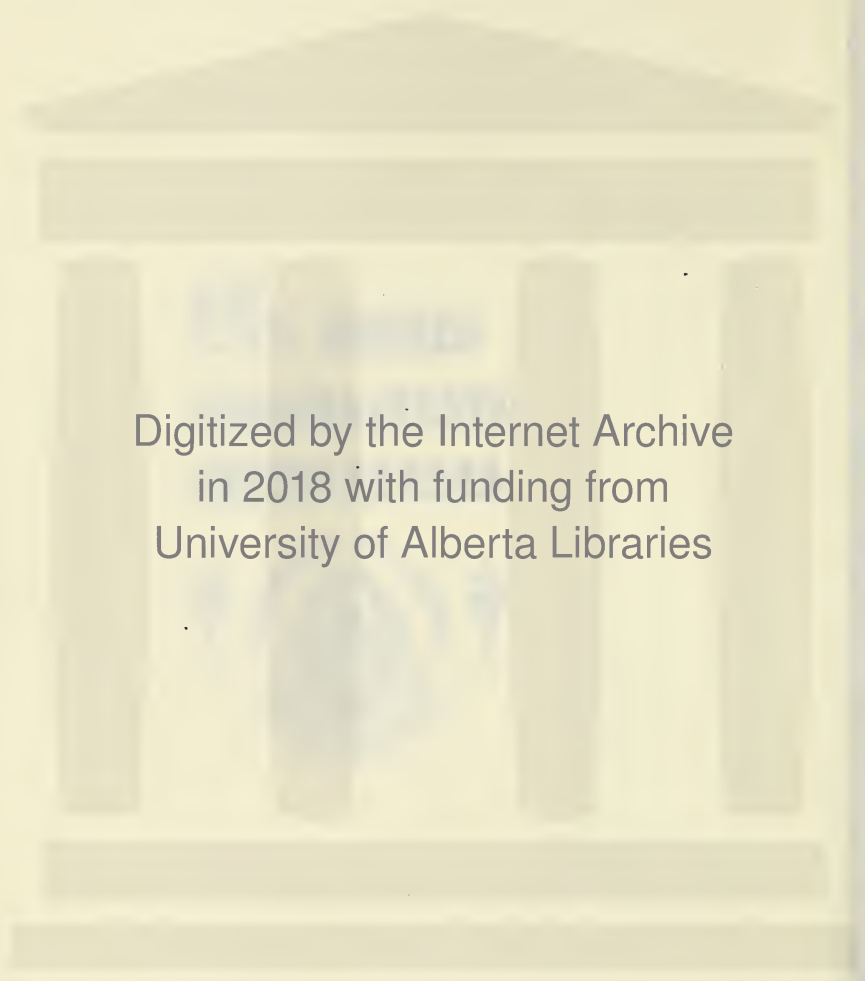
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UNIVERSITY OF ALBERTA
FACULTY OF AGRICULTURE

The undersigned hereby certify that they have read and recommended to the Committee on Graduate Studies for acceptance a thesis on "Solubility and Distribution of Phosphorus in Alberta Soils", submitted by William Odynski, B.Sc., in partial fulfilment of the requirements for the degree of Master of Science.

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SOLUBILITY AND DISTRIBUTION OF PHOSPHORUS
IN ALBERTA SOILS

William Odynski
University of Alberta

A THESIS
submitted to the University of Alberta
in partial fulfilment of the requirements for
the degree of
MASTER OF SCIENCE

Edmonton, Alberta

April, 1934

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SOLUBILITY AND DISTRIBUTION OF PHOSPHORUS

IN ALBERTA SOILS

W. Odynski

INTRODUCTION

This investigation was undertaken to obtain information regarding the nature and vertical distribution of the phosphorus compounds in certain typical Alberta soils by studying their solubility in acid solutions of varying concentrations.

Phosphorus occurs in soils in easily soluble and difficultly soluble forms, which are not due to the existence of two distinct compounds but of a large number of compounds of varying solubility. The estimation of the amounts of easily soluble and difficultly soluble forms of phosphorus has resulted in the adoption of many chemical methods depending on the use of different solvents approximating theoretically the concentration of the solvents found in close proximity to the plant roots. It is due to this consideration of the ease with which the phosphorus compounds of the soil may enter into solution that they have been divided into easily and difficultly soluble groups.

STUDYING AND INVESTIGATING IN SCIENCE
IN A SHORTER WAY

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There is considerable difference of opinion as to what phosphorus compounds belong to these groups. It is generally conceded, however, that the easily soluble group is composed of calcium phosphate chiefly, while the difficultly soluble group contains mainly iron phosphate, and in some cases organic phosphate. Considering the solubility of these compounds, it seems possible that by proper control of acidity a separation can be made of the easily and difficultly soluble forms on the basis of calcium and iron solubility. The forms in which these compounds are found may vary in different soils, and have a different solubility. Hence a determination of the rate of solubility seems of as great importance as the determination of ease of solubility.

In consideration of the problem outlined above, an attempt was made to determine the relative amounts and rate of solubility of the easily soluble and difficultly soluble phosphates occurring in Alberta soils. This was done by repeatedly extracting samples of all horizons at controlled pH values. An attempt was also made to determine the amount of phosphorus existing in organic combination in these soils. This investigation was conducted in the hope that the results of such attempts might add to our knowledge of the nature and distribution of the phosphorus compounds in soils.

LITERATURE REVIEW

Forms of Phosphorus Occurring in Soils. Phosphorus occurs in the liquid and solid phases of all soils. A very small amount is found in the liquid phase as compared to the much larger proportion existing in the solid phase. Both organic and inorganic forms of phosphorus are known to be present.

In his comprehensive review of the literature Hibbard (16) points out that mineral phosphate possibly occurs in the soil as apatite, $\text{Ca}_3(\text{PO}_4)_2\text{CaF}_2$; chlorapatite, $\text{Ca}_2(\text{PO}_4)_2\text{CaCl}_2$; hydroxyapatite, $(\text{Ca}_3(\text{PO}_4)_2)_3\text{Ca}(\text{OH})_2$; wagnerite, $\text{Mg}_3(\text{PO}_4)_2\text{MgF}_2$; magnesium phosphate; wavellite, $4\text{AlPO}_4 \cdot 2\text{Al}(\text{OH})_3 \cdot 9\text{H}_2\text{O}$ and aluminum phosphate. According to Bassett (5) hydroxyapatite is probably the chief source of soil phosphate.

Leahey (19) more recently found no evidence of the existence of crystalline iron phosphates in the soil and concluded that crystalline phosphates are not formed under normal soil conditions. Certain calcium phosphates may persist in a soil to a considerable extent under leaching conditions. The iron phosphates are very basic and complex in nature, being more basic than any phosphorus minerals so far reported. He further states that apatite inclusions are so rare in some soils that they need not be taken into

consideration as a factor in studying the insoluble phosphates in such soils.

Certain organic compounds containing phosphorus have been isolated from the soil. Page (24) and Teakle (35) mention the studies of some European workers who have described the isolation of nuclein and lecithin in small amounts, and others who have claimed the separation of organic forms of phosphorus from the ammonia extract of soils. Although the inaccuracies of the methods of separation are apparent, it cannot be overlooked that a large proportion of the phosphorus in the surface horizons is held in organic combination.

Solubility of Soil Phosphorus. Numerous procedures have been developed for the estimation of easily soluble phosphorus in the soil. Hibbard (16) points out that probably the most popular method is the weak acid extraction, with the sulfuric acid method of Truog (37) finding preference by many workers on this continent, whereas citric acid has found favor abroad. Any laboratory method that might be proposed for this purpose is more or less arbitrary, and considerable discussion has arisen as to what constitutes the easily soluble phosphorus. The problem is further complicated by the fact that these easily soluble and difficultly soluble phosphorus compounds are not sharply distinct. Hall

classification as a factor in estimating the intensity

characteristics in such cases.

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above mentioned classification of the cases.

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method of classification is not intended to be

applied to the cases of the above mentioned

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Classification of the cases.

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and Plymen (14) and Hall and Amos (13) long ago showed this to be true and brought forth the belief that there exist a large number of compounds of different degrees of solubility. When soils were repeatedly extracted with citric acid the solubility curves could not be fitted by any of the ordinary equations. In fact it can be taken as established that the reaction of acids on soils is not of the simple type presented by the familiar mono, di, or tri molecular reactions.

The investigations of Von Wrangell and his co-workers, as reviewed by Hibbard (16) and Lohse and Ruhnke (21), show that the soil phosphates must be largely of a very complex nature and their solubility is far less than that of the synthetic tertiary calcium and magnesium phosphates and the synthetic phosphates of aluminum and iron. They point out that the laws of diffusion do not govern the dissolution rate of these phosphates, but that the dissolution rate is governed by the rate of decomposition of the surface of the particles which contain the phosphate.

In the extraction of the easily soluble phosphorus of soils it would appear desirable to use a solvent which is approximately the same strength as the one operating in plant feeding. The evidence as pointed out by Truog (37) indicates that the solvent operating at the points of contact between root hairs and soil particles is a saturated solution of carbonic acid. This solution has a pH of about 3.7 and in an attempt to approximate this solvent Truog uses a

0.002N sulfuric acid solution buffered with ammonium sulfate to a pH 3.

The acidity of the solvent usually decreases somewhat during the extraction process as it comes in contact with the soil, due to the solution of bases, while in the case of plant feeding the solvent is continually being recharged by the excretion of additional carbonic acid by the roots. Bearing this in mind it seems quite important that, to get a proper conception as to the amount of phosphorus soluble at any pH, one must, as has recently been emphasized by Hibbard (16) and Lohse and Ruhnke (21) take great care to have the pH of the extract so adjusted that it will be the same for all soils. Lohse and Ruhnke (21) have recently suggested the use of KHSO_4 as solvent, claiming that by so doing, pH could be controlled much easier.

The solubility of the phosphates commonly existing in soils is to a large extent dependent on the acidity of the extracting solution (3,4,7,15,35).

Lohse and Ruhnke (21) give the following summary of Gaarder's investigations on the behavior of some of the most important phosphates found in soils:

					pH range of minimum solubility
Excess	of	iron hydroxide			3 - 4
"	"	aluminum hydroxide			5 - 6
"	"	"	"	+ Ca	5 - 6.3
"	"	"	"	+ Mg	4.6 - 6.5

In these pH ranges the phosphates are practically completely precipitated. However, since the ratios of each base to others and to phosphorus is different in different soils, each soil will act differently towards phosphorus solubility, even at the same pH value (30).

The behavior of phosphorus in soils is seen to be dependent to a large extent on the inherent differences of soils. In many cases complete solubility of soil phosphorus cannot be brought about by acid extractions. This insolubility of phosphorus in soils, Austin (4) points out, cannot be due solely to the soil reaction or the content of iron or aluminum, but must be due, at least in part, to yet unknown factors.

The studies on the precipitation of phosphates tend to show that reprecipitation of dissolved phosphate may take place during extraction of phosphate from soils if the soil remains in contact with the extract for a long time, and the pH of the solvent is above about a pH of 3. Such reprecipitation has been shown to take place by Russell and Prescott (28) in their studies on the action of dilute acids on phosphorus compounds in soils. Reprecipitation was most marked for dilute HNO_3 , less for HCl and least for H_2SO_4 . This variation as to the amount brought in by these various acids was attributed to be due to a physical adsorption. However, Comber (6) disagrees with these workers and

in these cases the Commission has specifically recommended
protection. However, since the degree of soil loss is
different and the measures to be taken are different, the
Commission will not recommend a single measure for all
cases of soil loss (1).

The Commission is of the opinion that it will be best to
proceed in a series of steps on the following lines:
first, to carry out a preliminary survey of soil
losses in the area concerned; secondly, to make a
detailed study of the causes of soil loss; thirdly,
to carry out a detailed study of the soil losses
in the area; fourthly, to make a detailed study of the
measures to be taken; fifthly, to make a detailed study
of the results of the measures taken.

The Commission is of the opinion that it will be best to
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in the area; fourthly, to make a detailed study of the
measures to be taken; fifthly, to make a detailed study
of the results of the measures taken.

attributes such reprecipitation as being of a strictly chemical nature, and that physical adsorption plays no part in the reaction.

Vertical Distribution of Soil Phosphorus. Few investigations reported in literature deal with the vertical distribution of soluble phosphorus. A large number deal with the distribution of the total amount of phosphorus in different horizons of soils (2,18,26,41). However, the total analysis gives very little information concerning the nature and movement of the soil phosphates in the horizons.

In studying some of the loess soils of Nebraska, Alway and Isham (1) showed that the amount of soil phosphates dissolved in 1 per cent citric acid extracts in the humid zone increased markedly from the first to the sixth foot, whereas in the arid portion a marked decrease from the surface downward was found. However, it is important to note that the presence of carbonates in the subsoils of the arid area tended to reduce the effect of the acid, for where these were destroyed before extraction the sixth foot horizon contained as much soluble phosphate as did the first foot horizon.

Dunnewald (9) using 0.001N H_2SO_4 studied the distribution of available phosphorus in Wyoming soils and concluded that available phosphorus decreases in the lower

At present, the investigation is being carried out in the field, and the results will be published in the near future.

Vertical Distribution of Soil Temperature

Vertical temperature profiles in the soil were determined at various depths in the field. The results show that the temperature decreases with increasing depth. The temperature at the surface is about 15°C, and at a depth of 10 cm it is about 10°C. At a depth of 20 cm, the temperature is about 8°C, and at a depth of 30 cm it is about 7°C. The temperature at a depth of 40 cm is about 6°C, and at a depth of 50 cm it is about 5°C. The temperature at a depth of 60 cm is about 4°C, and at a depth of 70 cm it is about 3°C. The temperature at a depth of 80 cm is about 2°C, and at a depth of 90 cm it is about 1°C. The temperature at a depth of 100 cm is about 0°C.

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Horizontal Distribution of Soil Temperature

Horizontal temperature profiles in the soil were determined at various depths in the field. The results show that the temperature decreases with increasing depth. The temperature at the surface is about 15°C, and at a depth of 10 cm it is about 10°C. At a depth of 20 cm, the temperature is about 8°C, and at a depth of 30 cm it is about 7°C. The temperature at a depth of 40 cm is about 6°C, and at a depth of 50 cm it is about 5°C. The temperature at a depth of 60 cm is about 4°C, and at a depth of 70 cm it is about 3°C. The temperature at a depth of 80 cm is about 2°C, and at a depth of 90 cm it is about 1°C. The temperature at a depth of 100 cm is about 0°C.

soil zones of all the profiles studied, as compared with the surface zones having organic matter accumulation. He further adds that the amount of lime increases in the lower zones to such an extent that the action of the acid is neutralized, with the result that very little phosphorus is brought into solution. In a more recent paper (10) he concludes that available phosphorus is more rapidly lost from the surface from grass soils than from podsolized timber soils.

Recent work by Stephenson and Chapman (33) and by Thor (36) shows that readily soluble phosphate added to the soil, can penetrate appreciably below the surface foot in light to medium textured soils, while little or no penetration seems to take place in very heavy soils. The readily soluble phosphate of manure seems to move more readily through soil.

Lohse and Ruhnke (22) in a very recent investigation using KHSO_4 at pH 2 conclude that surface sampling alone is inadequate and point out the extreme desirability of controlling and adjusting pH so that extracts from all horizons are of the same pH. They show that sandy podsoles seem to be very low in readily soluble phosphate in all horizons, that clayey podsoles and brown forest soils contained large amounts of readily soluble phosphate in the B horizon,

and in the parent material, and that the cultivated soils of the brown forest group contained, in all cases, considerable amounts of easily soluble phosphate in the lower horizons.

Effects of Ignition on Solubility of Phosphorus.

As pointed out by Stewart (34) it has long been known that simple ignition increased the solubility of phosphorus in cold hydrochloric acid. The increased solubility was for a long time believed to be due to the destruction of the organic phosphorus compounds. Furthermore, the amount of organic phosphorus as determined by ignition differed considerably from the amount found by ammonia extraction or by calculation from other analyses. Due to such differences he believed that ignition might have rendered some of the organic phosphorus insoluble in cold HCl at any strength.

Shortly after, Fraps (12) in investigating the effects of simple ignition on various phosphate rocks concluded:

(1) That ignition greatly increased the solubility of these rocks, such increases varying with the type of rock.

(2) That ignition of a soil would probably render inorganic phosphates soluble in acid, and was therefore not a method for estimating organic phosphorus.

(3) That evidence indicated that ignition of a soil rendered considerable quantities of iron and aluminum oxides soluble in acid.

A little later Lipman (20) in investigating the effect of heating soils at a low red heat for twenty minutes and then digesting with HNO_3 , found that ignition of soil appeared to decrease appreciably and definitely the solubility of its PO_4 whether it be organic or inorganic. He believed this to be due to the fact that soil is a complex mass and that its particles would be protected from heat so long as water of hydration and organic matter still remained in soil, hence no additional surface was exposed. Such dehydration of organic matter as well as of inorganic phosphates would seem to make them less soluble.

Recently Marais (23) has put forth the belief that in igniting the minerals, dehydration of the bases and destruction of crystalline structure tends to render the PO_4 more soluble or available to plants. However, it is pointed out that this belief alone cannot explain the peculiar and varied behavior of some mineral phosphates in giving up their PO_4 after heating. The work of Quartaroli is cited in attempting to explain this behavior on the basis of an existence of isomeric structures for mineral phosphates. Ignition may or may not alter the existence of the various isomers and so exert its effect on the solubility of the

(1) The first of these is the fact that the
the various conditions mentioned in the text are
not always satisfied in reality.

(2) The second is the fact that the
effect of the various conditions mentioned in the text
is not always the same, and that the conditions
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conditions mentioned in the text will not always be
satisfied in reality. It is therefore to be expected
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not always be satisfied in reality.

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the various conditions mentioned in the text are
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not always be satisfied in reality. It is therefore
to be expected that the effect of the various
conditions mentioned in the text will be different
in different cases, and that the conditions
mentioned in the text will not always be satisfied
in reality.

various phosphates.

Ford's study (11) showed that ignition of soils destroyed their fixing power to varying degrees with the accompanying liberation of phosphorus. Such variations as might exist in this respect he attributed to the presence of the various different behaving minerals. On ignition the dehydration of Goethite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) produced hematite (Fe_2O_3) and thereby destroyed its fixing power. Partial dehydration of bauxite ($\text{Al}_2\text{O}_3 \cdot \text{xH}_2\text{O}$) increased its fixing power and further dehydration did not entirely destroy it.

In recent investigations Doughty (8) found that the increase in soluble phosphorus was to a large extent dependent on the temperature at which the soils were ignited. Heating also tended to increase the pH value of the soils in all cases.

EXPERIMENTAL

The following experiments were designed to obtain evidence on the solubility of soil phosphorus throughout the different horizons of typical Alberta soils. The soil samples were repeatedly extracted with strong and weak acids until only traces of phosphorus were dissolved. On

various theories.

World's study (1) shows that factors of soils

destroyed their living power of neutral bacteria with the

consequently affected of themselves. This is because of

about water in the ground is polluted by the bacteria

of the various bacteria, bacteria, bacteria, bacteria, bacteria

destruction of bacteria (bacteria) bacteria, bacteria, bacteria

and thereby destroyed the living power. Bacteria, bacteria, bacteria

of bacteria (bacteria, bacteria) destroyed the living power and

thereby destroyed the living power and

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the bacteria is bacteria, bacteria, bacteria, bacteria, bacteria

destruction of the bacteria, bacteria, bacteria, bacteria, bacteria

destruction of the bacteria, bacteria, bacteria, bacteria, bacteria

in all cases.

CONCLUSION

The following statement was made by the author

conclusion - The bacteria of all bacteria, bacteria, bacteria

the bacteria, bacteria, bacteria, bacteria, bacteria, bacteria

samples have been destroyed, bacteria, bacteria, bacteria, bacteria

and will only be found in bacteria, bacteria, bacteria, bacteria

the basis of the amounts of phosphorus thus extracted an attempt was made to determine the relative proportions of calcium, iron and organic phosphorus in these soils.

Description of Soils

The soils used in this investigation are typical of the more mature soils of the gray wooded, the black and the brown soil belts of Alberta. These soils have been described in considerable detail (17,18,40,41) and only brief mention need be given of them here.

In the south of the province are the brown soils occurring in an area of low precipitation and high evaporation, and as a result characterized by relatively thin A and B horizons with the lime accumulation zone close to the surface. The A₂ and the B₁ horizons are not always easily distinguished from each other, and are often referred to as the B₁ horizon. The B₂ or lime horizon often occurs at less than a foot from the surface. The horizons are neutral to slightly alkaline in reaction. Occurring as they do in regions of low precipitation and high evaporation, there is not an excessive growth and accumulation of organic matter. Such salts that may accumulate do so near the surface, for percolation is quite shallow.

In the moister regions of part of central Alberta are produced the black soils, characterized by a deep very dark colored surface layer. This layer, the A_1 , has an average depth of about 10 inches. The A_2 and B_1 horizons are generally well developed and easily distinguished, and the B_2 horizon usually occurs at about three to four feet from the surface. The horizons exhibit a nearly neutral reaction. Due to a lower evaporation and a slightly greater downward movement of water, together with the active grass growth that is usually the main covering, there is a greater movement of the more soluble constituents, as is shown by the considerably lower carbonate horizon.

The wooded soil belt lying to the west and north of the main black soil belt, is fairly heavily wooded for the most part. The soils of this belt compose about two-thirds of the area of the province. They are the least fertile of the groups and are produced under more humid conditions than the other two. Characteristic of this group of soils is their apparently badly leached zone near the surface. The upper inch or two of these soils consists of leaf mould - the A_0 horizon. Immediately below this one finds a drab colored layer one or two inches thick - the A_1 horizon. The A_2 horizon is a light gray structureless soil having a characteristic ashy appearance, and shows signs of bad leaching.

In the present position of part of central Japan
and around the river, characterized by a high level
dark colored surface layer. This layer, on the other
average about 10 inches, and is of brownish
and generally well developed and easily distinguished, and
the surface usually occurs at about 1000 to 1200 feet
from the surface. The surface which is usually
reaction. Due to a lower elevation and a slight increase
movement of water, resulting in the surface
growth that is usually the main covering. There is a
movement of the water which is usually, as is shown by
the immediately lower surface level.
The second soil level is the soil level
of the main black soil level, is fairly heavily covered by
the main part. The soil of this level is usually about two
inches at the base of the surface. They are the same
side of the surface and are produced under water level
than the other two. Characteristic of this group is that
is fairly generally well located some near the surface.
The main part of two of these soils is usually of dark color -
the A₂ horizon. Immediately below this is the A₃ horizon.
colored layer one or two inches thick - one of brownish. The
A₃ horizon is a light grey silty clay, and shows signs of bad leaching.
characteristic with exposure, and shows signs of bad leaching.

This layer varies in thickness from 8 to 12 inches. The B₁ horizon below this is very heavy in texture and in some cases constitutes a hardpan. It is often several feet thick. The B₂ horizon of lime accumulation is seldom found less than about four feet from the surface. The soils of this group, bush covered as they generally are, are maintained in a humid condition, thus providing water for leaching purposes. The carbon dioxide produced from decaying organic matter renders this water slightly acidic, thereby increasing its leaching power and facilitating the downward movement of bases. There is a horizon in the upper part of the soil profile where a removal of bases and colloids has occurred with subsequent precipitation farther down.

For the present investigation two profiles were taken from the wooded area, two from the black and one from the brown. Those from the wooded area were taken at Breton and at Fallis, those from the black soil area were taken at Stony Plain and at Beaumont, and the brown profile was obtained at Provost.

Methods of Analysis

Sampling. The samples were obtained from natural horizons wherever possible. Where this was found difficult,

the samples were taken at arbitrary depths corresponding to the changes in color and texture. They were air dried on arrival at the laboratory and when air dried, were ground to pass a 20-mesh sieve.

Reaction. The pH values of the soil samples were determined in 1:4 extracts. The quinhydrone electrode was used in all cases.

Total Phosphorus. The total phosphorus was determined colorimetrically by first fusing the sample with sodium carbonate and then extracting with water according to the method developed by Truog and Rothermel[#].

Extraction. One gram samples were shaken one hour with 200 cc. solvent and filtered through a Buchner funnel. Phosphorus-free filter paper was used. The soil was repeatedly extracted till only traces of phosphorus were dissolved. After each filtration the filter paper and soil were returned to the shaker bottle and fresh solvent added.

Easily Soluble Phosphorus. The easily soluble phosphorus was extracted by the use of 0.002N H_2SO_4 buffered with $(\text{NH}_4)_2\text{SO}_4$ to pH 3 (37). The pH determinations in all extracts were made by means of the quinhydrone electrode and the phosphorus dissolved was determined by the Denigès

[#] Unpublished work.

method as modified by Truog and Meyer (38).

It is a matter of considerable controversy as to what may be termed easily soluble phosphorus. For the purposes of this investigation, it seemed most logical to separate the easily soluble from the difficultly soluble groups on the basis of iron solubility, since most investigators consider that iron phosphate is difficultly soluble (4,7,9,15,16,21,35,37). In most soils the easily soluble phosphorus exists largely as calcium phosphate, while the difficultly soluble exists largely as basic ferric phosphate (37). With this in mind samples of limonite were treated with H_2SO_4 solutions of different acidity to determine at what pH the iron was dissolved. The samples were shaken with extracting solution for one hour and then the solubility of the iron was determined by testing the filtrate on a spot plate with KCNS.

Table 1

Solubility of limonite in dilute H_2SO_4

At pH	2.8	2.7	2.6	2.5	2.4	2.3	2.2	2.1
Solubility of Fe	-	-	?	?	trace	+	++	+++

The results of Table 1 show no iron dissolved at pH 2.8 and pH 2.7, doubtful traces at pH 2.6 and pH 2.5 and increasingly positive traces at the lower pH values.

A similar study was made of a soil sample which had previously shown indications of high iron content. The sample selected was the Breton upper B₁. One gram samples were extracted by solutions of different pH and the amounts of iron and phosphorus in the extracts were determined. Repeated extractions were made in an attempt to determine at what rate the iron and phosphorus were being dissolved. The results, given in Table 2, show a much smaller amount of phosphorus and iron soluble at pH 2.9 than at pH 2. With increased acidity there is a distinct increase in their solubility. The amount of phosphorus dissolved at pH 2.9 is only 17 p.p.m. in the first extract with no decrease in the two subsequent extracts. The amount increases with increased acidity till at pH 2, 67 p.p.m. are found in the first extract and a more rapid decrease in the subsequent extracts. Thus the amount soluble and rate of solubility are definitely dependent on the acidity of the solvent. The amount of iron in solution in the first extract (Table 2) increases from a trace at pH 2.9 to 160 p.p.m. at pH 2. This amount decreases in the second and third extracts, although the decrease is much slower than in the case of phosphorus.

The results of the 1954-55 season are shown in Table 1.

In 1954 and 1955, the results of the 1954-55 season are shown in Table 1.

A similar result was also obtained in 1955-56.

The results of the 1955-56 season are shown in Table 1.

The results of the 1956-57 season are shown in Table 1.

The results of the 1957-58 season are shown in Table 1.

The results of the 1958-59 season are shown in Table 1.

The results of the 1959-60 season are shown in Table 1.

The results of the 1960-61 season are shown in Table 1.

The results of the 1961-62 season are shown in Table 1.

The results of the 1962-63 season are shown in Table 1.

The results of the 1963-64 season are shown in Table 1.

The results of the 1964-65 season are shown in Table 1.

The results of the 1965-66 season are shown in Table 1.

The results of the 1966-67 season are shown in Table 1.

The results of the 1967-68 season are shown in Table 1.

The results of the 1968-69 season are shown in Table 1.

The results of the 1969-70 season are shown in Table 1.

The results of the 1970-71 season are shown in Table 1.

The results of the 1971-72 season are shown in Table 1.

The results of the 1972-73 season are shown in Table 1.

The results of the 1973-74 season are shown in Table 1.

The results of the 1974-75 season are shown in Table 1.

TABLE 1

Table 2

The soluble iron and phosphorus in samples of Breton upper B₁ horizon extracted at different acidities

(expressed as p.p.m. on basis of dry soil)

1st Extract			2nd Extract			3rd Extract		
pH	P	Fe [#]	pH	P	Fe	pH	P	Fe
2.0	67	160	1.9	28	160	1.9	7	160
2.1	59	160	2.1	28	160	2.1	8	100
2.3	50	160	2.3	27	160	2.3	9	80
2.5	35	80	2.5	30	80	2.5	13	trace
2.6	35	trace	2.6	21	trace	2.6	9	"
2.7	29	"	2.7	19	"	2.7	11	"
2.8	22	"	2.8	22	"	2.8	11	"
2.9	17	"	2.9	17	"	3.0	13	--

Although H₂SO₄ at pH 2 dissolves the phosphorus more rapidly than do the less concentrated solutions it seems unsatisfactory for separating the easily soluble from the difficultly soluble soil phosphorus, since at this pH considerable amounts of iron are dissolved. Furthermore, the preliminary work as shown in Table 2 indicates definitely that regardless of what strength solvent is used, the first extraction alone is not sufficient to remove all of the easily soluble phosphorus, and the relative solubility or the phosphorus supplying power of a soil cannot be determined except by repeated extractions of the sample.

Fe means in this paper Fe⁺⁺⁺

Other preliminary experiments on the Stony Plain, Provost and Breton profiles showed that pH 2 solvents removed the phosphorus in four extracts and the pH 3 in six extracts (on the average). Although the total phosphorus removed in the Stony Plain and Provost horizons was practically the same for pH 2 as for pH 3 extraction, yet definite amounts of iron were found to be soluble at pH 2 in all horizons and notably in the subsurface ones. However, in the Breton profile there was a definite increase in the total phosphorus extracted at pH 2 as compared to that extracted at pH 3. This increase was accompanied by a pronounced increase in total iron dissolved. This profile was further investigated and extraction made of all horizons at pH 2.8. The total phosphorus extracted at pH 2.8 was virtually the same as at pH 3, yet at pH 2.8 definite traces of iron were dissolved in horizons below the A₁ horizon.

The length of time that the sample is shaken seems to have a considerable influence on the amount of phosphorus dissolved. Table 3 shows, in one case in particular, (Beaumont B₁) that one hour shaking was more effective than half hour shaking as recommended by Truog (37). Though minor differences occurred in the amount of phosphorus extracted in the other samples, the data (Table 3) indicate that the number of extractions might be reduced by shaking for the longer period.

These results are reported in the table below.

From the above results it is evident that the following factors are important in the determination of the rate of reaction:

(a) The concentration of the reactants.

(b) The temperature of the reaction.

(c) The nature of the catalyst.

(d) The surface area of the solid reactants.

(e) The pressure of the gaseous reactants.

(f) The time of contact between the reactants.

(g) The nature of the solvent.

(h) The nature of the reaction medium.

(i) The nature of the reaction vessel.

(j) The nature of the reaction conditions.

(k) The nature of the reaction products.

(l) The nature of the reaction mechanism.

(m) The nature of the reaction rate.

(n) The nature of the reaction order.

(o) The nature of the reaction equilibrium.

(p) The nature of the reaction kinetics.

(q) The nature of the reaction thermodynamics.

(r) The nature of the reaction stoichiometry.

(s) The nature of the reaction enthalpy.

(t) The nature of the reaction entropy.

(u) The nature of the reaction Gibbs free energy.

(v) The nature of the reaction activation energy.

(w) The nature of the reaction transition state.

(x) The nature of the reaction intermediate.

(y) The nature of the reaction complex.

(z) The nature of the reaction product.

Table 3

The effect of time of shaking upon the amount of phosphorus dissolved from soils by repeated extraction at pH 3

(expressed as p.p.m. on basis of dry soil)

Soil	Time of shaking	p.p.m. phosphorus in extracts				
		1st.	2nd.	3rd.	4th.	Total
Beaumont B ₁	30 mins.	65		not repeated		
	1 hour	100	35	8	5	148
	2 hours	110	29	9	5	153
	4 hours	135	21	10	4	170
A ₁	30 mins.	79	28	20	15	142
	1 hour	80	29	16	10	135
Provost B ₁	30 mins.	152	73	36	18	279
	1 hour	164	65	24	13	266
B ₂	30 mins.	277	60	37	16	390
	1 hour	275	65	22	13	375

Care was taken, in controlling the acidity, to have the pH of all extracts virtually the same, that is pH 3 within limits of 0.2. To achieve this, it was necessary to determine, by preliminary trials, the additional amount of acid required to neutralize the excess bases or lime present in samples of certain horizons. The acid used for this purpose was 1N H₂SO₄. Such additions of acid were required in only the first extracts of these samples.

The extract from the surface horizons was slightly colored due to organic matter coming into solution. This

coloring was somewhat objectionable, in some cases, in the colorimetric determination of phosphorus. In attempting to overcome this objection, the samples were filtered through a layer of carbon black.

The carbon black was previously purified by digesting with 2N HCl on a steam bath overnight. It was then filtered by suction till free of chlorides, thereby getting rid of most of the inorganic phosphorus that might have been present. The mass was then washed several times with a normal solution of NH_4OH to get rid of any adsorbed phosphorus that might be present, and to neutralize any remaining acid. When filtration had been completed the mass was transferred and dried at 100°C . for about two hours, and then heated in the muffle at 500°C . for five minutes to activate the carbon. This prepared carbon black was free of phosphorus and did not affect the pH of the extract.

A study was made to determine the amount of organic phosphorus dissolved at pH 3. Aliquots of the extracts were treated with 1 cc. of 10 per cent $\text{Mg}(\text{NO}_3)_2$, evaporated and the organic matter destroyed by ignition (25).

The data in Table 4 show that very small to negligible amounts of phosphorus in organic combination are soluble at pH 3. Carbon black, in decolorizing the solutions, shows negligible adsorption of the phosphate ion under the conditions of this experiment. The carbon black may have a

Table 4

Effect of the removal of dissolved organic matter by ignition and by carbon black upon the phosphorus content in pH 3 extracts of soils

(expressed as p.p.m. on basis of dry soil)

Soil (shaken for 30 mins.)	Phosphorus extracted		
	Organic matter not removed	Organic matter removed by carbon	Organic matter removed by ignition
Beaumont (Black) A ₁	23	24	30
Stony Plain (Black) A ₁ A ₂	165	165	170
	73	83	80
Fallis (Wooded) A ₀ A ₁ L. B ₁	180	175	190
	64	64	67
	175	174	168
Breton (Wooded) A ₀ A ₁	280	275	270
	100	100	97

greater affinity for other ions in solution (27) and, as a result, the adsorption of phosphate ions is negligible. The results of Table 4 further show that the removal of organic matter was not absolutely necessary in order to get comparable results. In all the soils studied the color of the extracts due to organic matter was not sufficiently

great to interfere with the determination.

Difficultly Soluble Phosphorus. The difficultly soluble phosphorus was extracted with 2N H_2SO_4 . A suitable aliquot was taken, neutralized with 1-1 ammonium hydroxide, made slightly acid and then analyzed by the modified method of Truog and Meyer (38). The increase in the total amount extracted by this solvent over that extracted at pH 3 represented the amount of difficultly soluble phosphorus.

Preliminary investigations showed that the solubility of the phosphorus compounds increased with increased strengths of acid. This increase was accompanied by a pronounced increase in the solubility of organic matter. Evidently the solvent for the difficultly soluble phosphorus should be of such concentration that a large amount of inorganic phosphorus and a small amount of organic phosphorus would be dissolved. Several concentrations of acid were tried and the amounts of organic and inorganic phosphorus dissolved were determined. The results of subsequent determinations are reported in Table 5.

The data of Table 5 show that the 5 per cent H_2SO_4 dissolved much more of the inorganic phosphorus than did the 1 per cent H_2SO_4 . Increased concentrations of acid resulted in

Table 5

Effect of acidity on the amount of inorganic and organic phosphorus dissolved from soils

(expressed as p.p.m. on basis of dry soil)

Strength of H_2SO_4 solvent	Breton A ₀		Breton A ₁		Stony Plain A ₁		Breton lower B ₂	
	Inor-	Organ-	Inor-	Organ-	Inor-	Organ-	Inor-	Organ-
	ganic	ic	ganic	ic	ganic	ic	ganic	ic
1% (.41N)	460	230	485	30	330	80	460	--
5% (1.72N)	530	455	570	230	370	95	420	--
10% (3.4N)	580	460	600	220	390	135	420	--
20% (8.06N)	680	370	685	250	390	220	460	--

smaller increases of soluble phosphorus in the surface horizons. The lime horizon, however, showed no increase in phosphorus dissolved by the more concentrated solvents. The amount of organic phosphorus dissolved, however, increased considerably. The increases in organic phosphorus dissolved in the Stony Plain profile seemed so much greater than the increases in inorganic phosphorus dissolved that the use of a solvent of greater concentration than 5 per cent H_2SO_4 was unwarranted. Further study, using .4N $KMnO_4$ to determine the amount of organic matter in solution, showed a narrower P:O.M. ratio in the 5 per cent extracts than in the others.

In view of these considerations a 2N solution of H_2SO_4 (approximately 5 per cent) was used for the extraction of difficultly soluble phosphorus.

The extracts obtained by using 2N H_2SO_4 were too acid for a direct colorimetric determination of phosphorus (38). They were neutralized with 1-1 NH_4OH using bromophenol blue, since this indicator shows color change in the range of pH 3 to pH 3.9. Preliminary experiments showed that neutralized samples taken from the same extract gave quite variable phosphorus readings. The variations seemed most pronounced when more of the extract, and hence more NH_4OH , was used. This variability on the part of neutralized samples was investigated by determining the effect of different amounts of NH_4OH on prepared standards of known phosphorus content.

Four different concentrations of H_2SO_4 were used. The samples for study were prepared by taking 10 cc. portions of acid, and adding 5 cc. of a standard phosphate solution to each. The mixture was neutralized by a predetermined amount of NH_4OH , made slightly acid, and then diluted to 100 cc. Phosphorus determinations were made in the ordinary way (38) and also by comparison with standards that had been prepared in the same manner as the samples.

The data of Table 6 show a decided variation in readings and a pronounced increase in such cases where more

Table 6

Effect of ammonium salts on the development of blue color in the modified Denigès colorimetric method for phosphorus.

Concentration of H_2SO_4 (10 cc. portions neutralized with NH_4OH)	Amount (cc.) of standard required to match 50 cc. of sample (results of several readings)	Amount (cc.) of treated standard required to match 50 cc. of sample (results of several readings)
1%	51,53,50,50	51,52,50,51
5%	55,56,56,48	50,51,52,51
10%	58,57,58,48	49,50,51,50
20%	62,63,56,50	54,50,52,51

NH_4OH was used (first column). The NH_4OH was found to be free of phosphorus and it may be that the ammonia salts formed in the neutralizing process have some distinct effect on the blue color developed. The intensity of the blue color may be increased, or more probably the greenish tints developed due to these ammonia salts may serve to intensify the blue color. Such intensification became more pronounced with an increase in the amount of NH_4OH used. Furthermore, the blue color in the neutralized samples showed a decided tendency to fade. In the method as developed by Truog there is very little fading of color in the first 10 minutes, whereas after treatment with NH_4OH the samples faded rapidly after 5 minutes, especially where larger amounts of NH_4OH were used.

When the standards were treated in the same way as the samples much better agreement of results was obtained

(column 2, Table 5). Thus by comparing only a few samples at a time with a standard containing about the same proportion of ammonia salts, it was possible to get much more consistent results. This method, of comparing with proportionally treated standards, was used to determine the phosphorus dissolved by 2N H_2SO_4 .

Soluble Iron. The soluble iron was determined in 50 cc. portions of the extracts by adding 5 cc. of 2 per cent KCNS and then comparing the color produced with prepared color standards (31).

Organic Phosphorus. The samples were ignited in an electric muffle furnace at $600^\circ\text{C}.$, for one hour, to destroy the organic matter. After cooling, they were repeatedly extracted in the same manner and with the same solvents as the unignited samples. The average increase in the amount of phosphorus dissolved after ignition, indicated the relative amount of organic phosphorus.

EXPERIMENTAL RESULTS

The reported results are the average of several duplicate readings. Where such results have been expressed as percentages, they have been calculated to the nearest whole number.

Easily Soluble Phosphorus

One extraction alone was not sufficient to remove all of the easily soluble phosphorus of a soil nor did it give complete information as to the rate of solubility of that phosphorus. The data of Table 7 show appreciable amounts of phosphorus dissolved after the first extraction. In the A_0 , A_1 , lower B_1 and B_2 of most profiles, over 50 per cent of the total extracted phosphorus was obtained in the first extraction, while in the upper B_1 horizons of the Fallis and Breton profiles the amount dissolved remained fairly constant for the first two and three extracts respectively.

The data for some horizons of the Breton profile are presented in Fig. 1 as being fairly typical of the different rates of solubility shown in Table 7. The graphical representation (Fig. 1) may perhaps serve better to show the variation in the amounts of phosphorus extracted from different horizons at different stages of the extraction. In all cases appreciable amounts were dissolved in the third and in some cases even in the fifth extraction. A decided potential source of the easily soluble phosphorus is present over and above that found in the first extraction. Furthermore, investigations conducted to show amounts of easily soluble phosphorus in soils should never be confined to the surface horizons alone because, as seen from Table 7, the subsurface horizons often contain considerable amounts of easily soluble phosphorus which may be utilized by deep rooted plants (39).

Table 7

Soil reaction, total phosphorus and easily soluble phosphorus
of Alberta soils

(expressed as p.p.m. on basis of dry soil)

Horizon	Depth in inches	Soil pH	Total# P in soil	Phosphorus in extracts							% of total # P. ex- tracted	
				1st.	2nd.	3rd.	4th.	5th.	6th.	7th.		Total ex- tracted
Provost (Brown)												
A ₁	0-6	7.1	606	73	29	16	10	8	--	--	136	22
B ₁	6-12	7.5	547	164	62	24	13	10	--	--	273	50
B ₂	18-24	7.9	518	275	65	22	13	11	--	--	386	75
C	40-43	7.2	513	250	56	29	20	8	--	--	363	71
Beaumont (Black)												
A ₁	0-15	6.5	939	40	34	14	8	--	--	--	96	10
B ₁	15-30	7.0	464	97	42	8	3	--	--	--	150	32
B ₂	30-36	7.4	603	290	108	41	12	5	--	--	456	76
C	at 54	7.4	509	300	71	26	12	7	--	--	416	82
Stony Plain (Black)												
A ₁	0-16	7.2	869	198	42	31	31	16	6	4	328	38
A ₂	16-24	7.0	575	115	44	30	24	14	5	6	238	41
B ₁	24-40	6.9	405	90	40	22	21	15	6	7	201	50
B ₁	at 40	7.0	391	120	38	18	15	6	4	--	201	51
B ₂	at 72	7.4	491	218	80	38	26	10	4	--	376	77

Total P. as determined by Na₂CO₃ fusion method (p. 16).

Table 7 (Continued)

Horizon	Depth in inches	Soil pH	Total P. in soil	Phosphorus in extracts							% of total P. ex- tracted	
				1st.	2nd.	3rd.	4th.	5th.	6th.	7th.		Total ex- tracted
Fallis (Wooded)												
A ₀	0-2	7.0	1106	166	37	19	12	15	4	--	253	23
A ₁	2-4	6.7	709	70	25	15	10	13	6	--	139	20
A ₂	4-12	6.2	351	55	26	18	8	8	3	--	118	34
B ₁	12-24	6.0	310	16	12	8	5	--	--	--	41	13
B ₁	36-60	7.0	383	183	35	12	7	4	--	--	241	63
B ₂	at 60	7.6	506	300	63	22	11	6	--	--	402	80
Breton (Wooded)												
A ₀	0-1	6.4	1730	294	55	29	18	25	10	--	431	25
A ₁	1-2	6.0	1305	110	53	37	25	26	16	--	267	20
A ₂	2-8	6.0	347	23	23	22	7	3	--	--	78	23
B ₁	12-24	5.4	325	16	17	16	6	3	--	--	58	18
B ₁	24-56	6.9	538	255	54	33	15	10	10	--	377	70
B ₂	56-72	7.5	589	283	91	36	17	10	4	--	441	75
B ₂	72-78	7.6	591	293	108	37	17	8	5	--	468	79

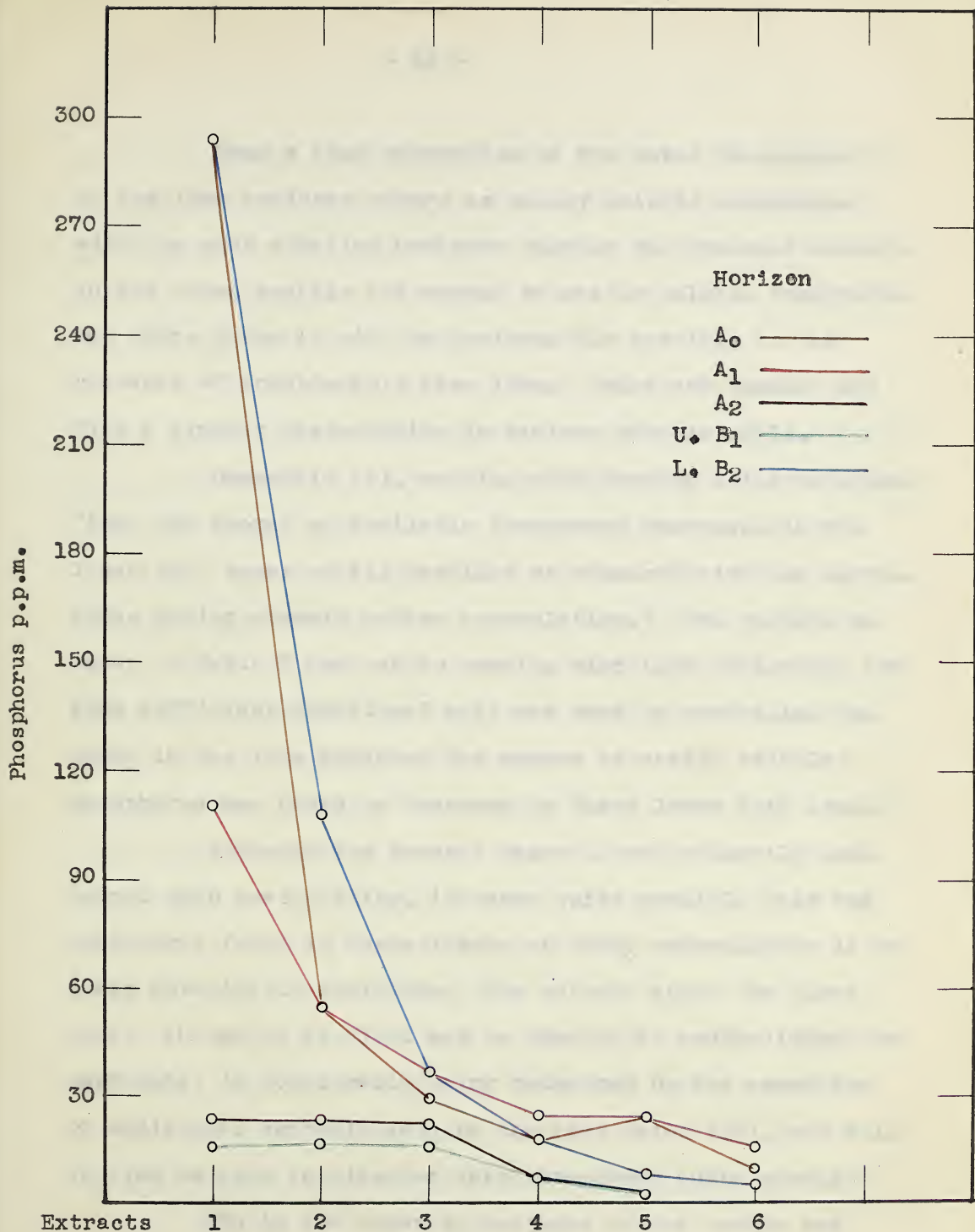


Fig. 1. Breton profile. Easily soluble phosphorus in repeated extracts of certain horizons.

Fig. 1. Graph showing the effect of the concentration of the solution on the rate of the reaction.



Thus a high proportion of the total phosphorus in the lime horizons occurs as easily soluble phosphorus with the most alkaline horizons showing the greatest amounts. In the brown profile the amount of easily soluble phosphorus was quite large in all the horizons due possibly to the presence of considerable free lime. Lohse and Ruhnke (22) find a similar distribution in various Ontario soils.

Dunnewald (9), working with Wyoming soils concluded "that the amount of available phosphorus decreases in the lower soil zones of all profiles as compared with the surface zones having organic matter accumulation." The results as shown in Table 7 are not in keeping with this statement, for when sufficient additional acid was used to neutralize the CaCO_3 in the lime horizons the amount of easily soluble phosphorus was found to increase in these lower soil zones.

Although the present paper is not primarily concerned with availability, it seems quite possible that the phosphorus found in these layers of CaCO_3 accumulation is at least potentially available. The solvent about the plant roots, though it at first may be used up in neutralizing the carbonate, is continually being recharged by the excretion of additional carbonic acid by the root hairs (37), and will in time be able to dissolve this phosphorus quite readily.

The A_2 and upper B_1 horizons of the Breton and Fallis profiles have a very low and slowly soluble amount of phosphorus extracted (Table 7). The A_2 horizon has been

severely leached, whereas the upper B_1 horizon has an accumulation of aluminum and iron brought down in the course of leaching (18). The greater part of the phosphorus present in these slightly acid horizons may be combined with aluminum and iron in difficultly soluble forms.

These A_2 and upper B_1 horizons of the Breton and Fallis profiles have likewise a low total phosphorus content. This low total may be due to an upward transference of phosphorus by the plants, or to a downward movement due to leaching. If the phosphorus had been leached to the lower horizons these should have a much higher total phosphorus content than the parent material horizons. Such was not the case, for the fairly constant total in the parent material layers was not appreciably lower than the total phosphorus content of the horizons immediately above. Similarly in the other profiles studied, except the Beaumont, there are no indications of any appreciable downward movement of native phosphorus. Leahey (18) also found very little evidence to indicate such downward movement.

Tests for iron were made on the extracts of all horizons. The tests showed no traces of iron in solution at pH 3 in the black and brown profiles. In the wooded profiles, however, traces of iron were found in the extracts of all horizons below the upper B_1 .

Effect of Ignition on the Amount of Phosphorus and Iron Dissolved at pH 3. In an endeavor to determine how much of the soil phosphorus occurred in organic combination, the samples were ignited and then repeatedly extracted at pH 3. The data in Table 8 show:

(1) In the upper, organic matter, horizons a pronounced increase in easily soluble phosphorus is found after igniting the samples. The total easily soluble phosphorus extracted after ignition is found to be at least twice as great as the total extracted from the unignited samples.

(2) In the intermediate horizons there is a small difference between the total extracted after ignition and the total extracted before ignition.

(3) In the lime horizons, ignition often causes a slight decrease in the amount of easily soluble phosphorus extracted.

In all cases (see Table 8) the differences in amount of easily soluble phosphorus are most pronounced in the first extracts. Further extractions show a marked decrease in the rate of solubility. More extractions are needed to reach the end point of phosphorus solubility after ignition than before, as shown by comparing the data of Tables 7 and 8.

Table 3: Results of the Survey of 1960-1961

and from 1960 to 1961. In the summer of 1960, the

the mean of the total population was 10,000,000.

During the period 1960-1961, the population was 10,000,000.

Table 3 shows the results of the survey.

(1) In the summer of 1960, the population was 10,000,000.

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Table 8

Effect of ignition at 600°C. on the amount of phosphorus dissolved from Alberta soils by repeated extraction at pH 3

(expressed as p.p.m. on basis of dry soil)

Horizon	P. in extracts								% of total P.	
	1st.	2nd.	3rd.	4th.	5th.	6th.	7th.	Total extract- ed	Ex-tract- ed at pH 3	Increase extract- ed at pH 3 after ignition
Provost (Brown)										
A ₁	248	58	37	23	18	12	9	405	67	45
B ₁	115	61	49	39	30	14	10	318	58	8
B ₂	103	79	60	47	31	14	9	343	66	- 9
C	148	65	51	31	21	15	10	341	66	- 5
Stony Plain (Black)										
A ₁	430	107	57	32	26	17	11	680	78	40
A ₂	200	59	40	26	21	14	10	370	64	23
U. B ₁	120	40	30	20	16	12	8	246	61	11
L. B ₁	110	33	21	15	10	--	--	189	48	- 3
B ₂	155	91	57	32	20	15	10	380	77	0
Breton (Wooded)										
A ₀	1243	190	80	50	29	20	11	1623	94	69
A ₁	575	152	80	51	35	25	17	935	72	52
A ₂	108	37	21	15	10	--	--	191	55	32
U. B ₁	68	24	17	14	9	--	--	132	41	23
L. B ₁	205	52	35	24	16	13	9	354	66	- 4
U. B ₂	250	80	52	33	19	17	12	463	79	4
L. B ₂	175	154	80	43	22	19	13	506	86	7

Several horizons of the Breton profile have been selected for Fig. 2 to typify the effects of ignition on the solubility of phosphorus in soils. The high organic matter A₁ horizon (as represented by the red lines) shows a greatly

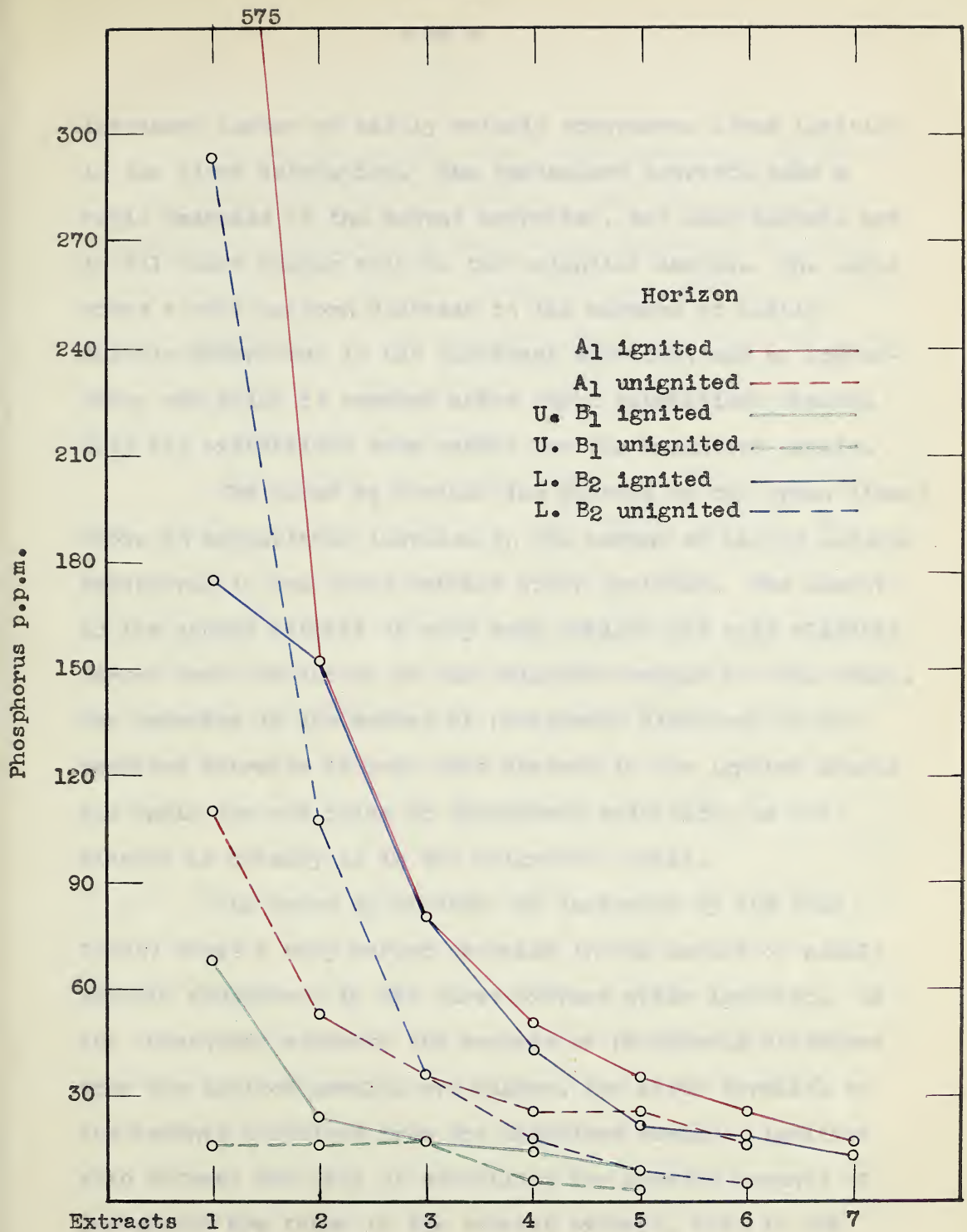
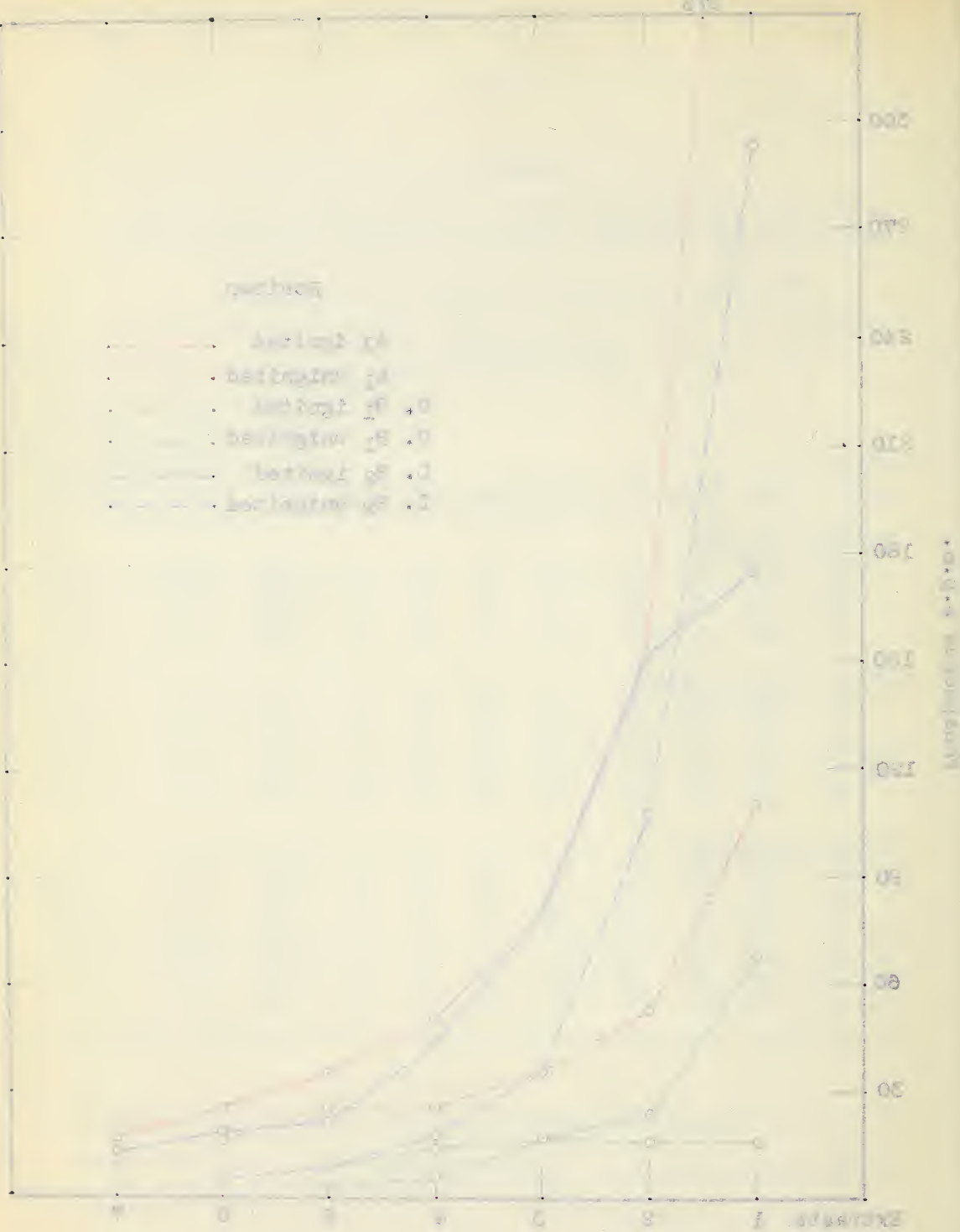


Fig. 2. Breton profile. Easily soluble phosphorus in repeated extracts of ignited and unignited samples of certain horizons.

Fig. 2. Breton model. Rapid relative response in response to changes of input and output.



increased amount of easily soluble phosphorus after ignition in the first extraction. The subsequent extracts show a rapid decrease in the amount extracted, but such amounts are in all cases higher than in the unignited sample. The curve shows a more uniform decrease in the amounts of easily soluble phosphorus in the different extracts, and an approximate end point is reached after seven extractions whereas only six extractions were needed for the unignited sample.

The upper B₁ horizon (as plotted by the green lines) shows an appreciable increase in the amount of easily soluble phosphorus in the first extract after ignition. The amount in the second extract is very much smaller and only slightly larger than the amount in the unignited sample at this stage. The decrease in the amount of phosphorus dissolved in the repeated extracts is much more gradual in the ignited sample and again the end point of phosphorus solubility is not reached as quickly as in the unignited sample.

The lower E₂ horizon (as indicated by the blue lines) shows a very marked decrease in the amount of easily soluble phosphorus in the first extract after ignition. In the subsequent extracts the amounts of phosphorus dissolved from the ignited samples are higher, but about parallel to the amounts dissolved from the unignited sample. Ignition also affects the rate of solubility for greater amounts of phosphorus are found in the seventh extract, than in the sixth of the unignited sample.

In the Provost B₂ and C, the Stony Plain lower B₁ and the Breton lower B₂ (Table 8) the total amount of phosphorus extracted at pH 3 was lower after ignition than before (Table 7). The soil particles appeared more granular after ignition and it was believed that such granulation of the fine particles might account for the decrease in the amount of phosphorus dissolved.

This effect was investigated by weighing out two gram samples of the Provost B₂, Stony Plain lower B₁ and Breton lower B₁ and igniting as before. After ignition the loss in weight due to ignition was calculated. The sample was then ground in an agate mortar and a portion equivalent to one gram of unignited soil was weighed out. Repeated extractions were made as previously outlined. The results given in Table 9 show that granulation has some slight effect on the solubility. The extracts showed about the same total amounts of easily soluble phosphorus in the pulverized as in the unignited samples with a slight increase noted in the Provost sample. The wide difference in the initial extracts of this Provost sample, where in the one case the extract was at pH 3.6 and in the other at pH 3.1, may be due to iron precipitating out the phosphorus, for even at pH 3.6 the calcium phosphate should be quite soluble (3,7,35). The low results obtained in the first extract may be due to the fact that at pH 3.6, with considerable excess of iron,

Table 9

Phosphorus dissolved, by repeated extraction at pH 3,
from soils pulverized after ignition

(expressed as p.p.m. on basis of dry soil)

Horizon	Adjusted pH of 1st. extract	Phosphorus in extracts								Total ex- tracted
		1st.	2nd.	3rd.	4th.	5th.	6th.	7th.	8th.	
Brown B ₂	3.6	22	94	92	82	33	29	20	15	387
	3.1	172	130	63	36	19	13	--	--	433
Stony Plain lower B ₁	3.1	128	35	25	18	13	10	--	--	229
Breton lower B ₁	3.1	202	80	38	28	18	12	9	--	387

pulverizing might have rendered it more easily available to combine with the dissolved phosphate and precipitate out as ferric phosphate which was insoluble at pH 3.6. However, at pH 3.1 the liberated ferric oxides would not have such a tendency to precipitate out as ferric phosphates, due to this higher acidity inhibiting such a reaction or rendering some of the thus freshly precipitated phosphates soluble.

Ignition seems also to have increased the alkalinity of the soil for twice as much of the 1N H₂SO₄ was needed to adjust the pH value of the first extract in all cases. In the Brown B₂ a further excess of 0.4 cc. over and above this amount was required to adjust the pH to 3.

An analysis of the extracts for iron showed distinct differences in the ignited and unignited samples. The data in Table 10 show that whereas very little or no iron is found in the pH 3 extracts of unignited samples, yet after ignition there is a distinct amount dissolved in all cases. The quantities of iron vary considerably, but it is significant to note that the largest amounts found are in horizons having considerable free lime, as in the brown profile. This same relationship holds in the other profiles, for after ignition the amount of iron dissolved is greatest in the lime horizons. In the upper horizons, and to some extent in the lower, this increase may be due to a liberation of iron tied up in the organic matter. No explanation is offered for the great increase in the lime horizons.

Upon pulverization more iron is dissolved. This is especially noticeable in the Brown B₂ horizon where at pH 3.6 very little iron is found in the first extract, but in subsequent extractions, where the pH is back to 3 again, greater amounts occurred. At pH 3.1 a very decided and significant increase in soluble iron is noted in the first extract. This fact may help to account for the peculiar difference in the solubility of the phosphorus in these two cases as shown in Table 9.

Table 10

The soluble iron in unignited, ignited and ignited-pulverized soils as determined by repeated extracts at pH 3

(expressed as p.p.m. on basis of dry soil)

Horizon	Un-ignited	Ignited				Ignited pulverized			
		1st.	2nd.	3rd.	4th.	1st.	2nd.	3rd.	4th.
<u>Provost (Brown)</u>									
A ₁	--	240	80	40	--				
B ₁	--	440	120	100	100				
B ₂	trace	520	80	60	60	(160 [#]	560	320	160
C	"	160	--	--	--	(1040 ^{##}	280	80	40
<u>Stony Plain (Black)</u>									
A ₁	--	280	120	80	--				
A ₂	--	120	--	--	--				
U. B ₁	--	60	--	--	--				
L. B ₁	trace	60	--	--	--	240	--	--	--
B ₂	"	240	80	--	--				
<u>Breton (Wooded)</u>									
A ₀	--	280	120	120	80				
A ₁	--	240	160	160	80				
A ₂	--	60	--	--	--				
U. B ₁	trace	90	--	--	--				
L. B ₁	"	60	--	--	--	320	--	--	--
U. B ₂	"	60	--	--	--				
L. B ₂	"	360	60	40	--				

First extract at pH 3.6.
 ## " " " pH 3.1.

Since ignition has some definite effect on the solubility of the phosphorus the iron and possibly even the calcium, this method cannot be used to determine accurately the amount of organic phosphorus present in a soil. Yet in

Table 13

The following table shows the results of the analysis of variance for the different groups of subjects, and the results of the analysis of variance for the different groups of subjects, and the results of the analysis of variance for the different groups of subjects.

(continued on page 25)

Analysis of Variance									
Source of Variation									
Sum of Squares									
Degrees of Freedom									
Mean Square									
F Value									
Significance Level									
Probability									
Critical Value									
Observed Value									
Conclusion									
Remarks									
References									
Appendix									
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spite of its shortcomings, it is possibly indicative of the amount of organic phosphorus present in the various soil horizons, notably the surface horizons. With this in mind an estimate of the amount of organic phosphorus present may be obtained by subtracting the total phosphorus extracted after ignition from the total extracted without igniting. This has been done in the last column of Table 8. The A_0 horizon of the Breton wooded soil, composed chiefly of vegetable detritus, has approximately 70 per cent of its phosphorus in organic form. The A_1 horizons of all three soils show a variable content of from 40 per cent to 50 per cent of their phosphorus in organic combination. Below this horizon the decrease in organic phosphorus is rapid and characteristic of each soil. The brown profile shows 8 per cent of the total phosphorus as organic in the B_1 to 0 per cent in the B_2 and C. The Stony Plain on the other hand shows a more uniform decline of from 23 per cent in the A_2 , 10 per cent in the upper B_1 to 0 per cent in the lower two horizons. The Breton profile shows a somewhat greater proportion of the total phosphorus tied up with organic matter in that 32 per cent of the A_2 , 22 per cent of the upper B_1 , 0 per cent of the lower B_1 and 4 per cent to 7 per cent of the lower two horizons is organic phosphorus.

The total phosphorus extracted from the unignited samples (Table 7) may be considered fairly representative

of the relative amounts and distribution of calcium phosphate in Alberta soils.

Difficultly Soluble Phosphorus

The concentration of the solvent used to determine the difficultly soluble phosphorus was believed to be great enough to neutralize the excess bases or lime present in some horizons without appreciably affecting its normality. Hence all horizons were repeatedly extracted with 200 cc. of 2N H_2SO_4 and no additional amounts of acid were added. The results showing the amount of phosphorus dissolved in these repeated extracts are given in Table 11.

The data of Table 11 show that the phosphorus is dissolved more rapidly than in the case of pH 3 extraction (Table 7). However, the phosphorus dissolved in the first extraction with 2N H_2SO_4 is in many cases virtually the same as the total extracted at pH 3. This is especially notable in the lower B_1 , the B_2 , and C horizons. In the A_1 , A_2 and upper B_1 horizons of the wooded soils, however, a distinct difference is noted. The total amounts extracted with 2N H_2SO_4 show that the phosphorus is almost all extracted only in the B_2 and C horizons, whereas in the remaining horizons of the various profiles only 50 per cent to 75 per cent of the phosphorus is extracted. Further

Table 11

Phosphorus dissolved from Alberta soils by repeated extraction with 2N H₂SO₄

(expressed as p.p.m. on basis of dry soil)

Horizon	p.p.m. P. in extracts					% of total P. [#]	
	1st.	2nd.	3rd.	4th.	Total P extracted	Extracted by 2N H ₂ SO ₄	Increase extracted by 2N over pH 3
Provost (Brown)							
A ₁	185	15	8	--	208	34	12
B ₁	310	15	7	--	332	61	11
B ₂	385	17	6	--	408	79	4
C	388	16	6	--	410	80	9
Beaumont (Black)							
A ₁	125	11	7	--	143	15	5
B ₁	185	12	6	--	203	44	12
B ₂	505	17	4	--	526	87	11
C	455	22	6	--	483	95	13
Stony Plain (Black)							
A ₁	370	23	12	8	413	48	10
A ₂	255	20	10	9	294	51	10
U. B ₁	215	18	11	7	251	62	12
L. B ₁	215	19	10	7	251	64	13
B ₂	405	17	5	--	427	87	10
Fallis (Wooded)							
A ₀	330	29	15	10	384	35	12
A ₁	265	24	15	10	314	44	24
A ₂	175	18	9	7	209	60	26
U. B ₁	91	21	13	--	125	40	27
L. B ₁	275	17	10	--	302	79	16
B ₂	380	20	11	--	411	81	1
Breton (Wooded)							
A ₀	530	36	17	8	591	34	9
A ₁	610	42	18	11	681	52	32
A ₂	145	21	8	8	182	52	29
U. B ₁	137	20	12	8	177	54	36
L. B ₁	365	18	10	--	393	73	3
U. B ₂	455	19	9	--	483	82	7
L. B ₂	465	18	9	--	492	83	4

See footnote after Table 5.

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investigation revealed that even with strong acids it is highly improbable that the total phosphorus can be completely extracted, especially in the horizons containing relatively little or no free lime.

The increase in the amount of phosphorus extracted by $2N\ H_2SO_4$ over the amount extracted by H_2SO_4 at pH 3 (last column, Table 11) may be taken as representing the amount of difficultly soluble phosphorus here referred to as iron phosphate. This increase is fairly constant at about 10 per cent in all horizons of the brown soil, except the B_2 or lime horizon, where only 4 per cent of the total phosphorus is iron phosphate. In the Beaumont black soil about 12 per cent is iron phosphate in the B_1 and C horizons with much smaller amounts in the A_1 and B_2 horizons. The Stony Plain profile shows a more constant proportion of about 10 per cent with slight increases in the B_1 horizon. In the wooded profiles, however, where leaching has been more severe, a gradual increase in the proportion of iron phosphate occurs from the surface horizon to the lower B_1 . The upper B_1 horizon seems to have the heaviest concentration of iron phosphate, while in the horizons below it, the decrease is very rapid reaching almost negligible amounts in the B_2 or lime horizons.

The data (Table 11) indicate that where an excess of calcium carbonate is present the formation of calcium

phosphate is favored rather than the formation of iron phosphate.

Effect of Ignition on the Amount of Phosphorus and Iron Dissolved by 2N H₂SO₄. In an attempt to again determine the amount of phosphorus held in organic combination, the samples were ignited as before and then extracted, with 2N H₂SO₄. The data presented in Table 12 indicate that a very considerable portion of the phosphorus is held in organic combination in the surface horizons with a rapid decrease in the subsurface horizons. Several horizons of the Breton profile have been selected for Fig. 3 to typify the effect of ignition on the amount of phosphorus dissolved by 2N H₂SO₄. The high organic matter A₁ horizon (as shown by the red lines) shows a very great increase in soluble phosphorus in the first extract. The subsequent extracts show a rapid decrease in the amount extracted, yet these amounts are all higher than in the unignited sample. The upper B₁ horizon (as plotted by the green lines) shows an appreciable increase in the amount of phosphorus dissolved in the first extract. In the subsequent extracts the amounts decrease very rapidly but remain again higher than the amounts in the same extracts of the unignited samples. The lower B₂ horizon (as indicated by the blue lines) shows a slight increase in soluble phosphorus due to ignition in the first extract. In the subsequent

Table 12

Effect of ignition at 600°C. on the amount of phosphorus dissolved from Alberta soils by repeated extraction with 2N H₂SO₄

(expressed as p.p.m. on basis of dry soil)

Horizon	Phosphorus in extracts				% of total phosphorus	
	1st.	2nd.	3rd.	Total ex-tracted	Extract- ed by 2N H ₂ SO ₄	Increase ex-tracted by 2N H ₂ SO ₄ after ignition
<u>Provost (Brown)</u>						
A ₁	515	31	11	557	92	58
B ₁	485	27	9	521	95	34
B ₂	465	23	7	495	96	17
C	460	25	8	493	96	16
<u>Beaumont (Black)</u>						
A ₁	805	40	10	855	91	76
B ₁	335	23	8	366	79	35
B ₂	550	23	6	579	96	9
C	495	19	10	524	100	5
<u>Stony Plain (Black)</u>						
A ₁	740	37	11	788	91	43
A ₂	455	30	11	496	86	35
U. B ₁	305	21	9	335	83	21
L. B ₁	290	23	12	325	83	19
B ₂	475	18	10	503	100	13
<u>Fallis (Wooded)</u>						
A ₀	1070	35	11	1116	100	65
A ₁	590	36	16	642	91	47
A ₂	270	23	9	302	86	26
U. B ₁	215	25	8	248	80	40
L. B ₁	315	18	5	338	88	9
B ₂	485	19	5	509	100	19
<u>Breton (Wooded)</u>						
A ₀	1625	62	9	1696	98	64
A ₁	1065	63	13	1141	87	35
A ₂	290	20	6	316	91	39
U. B ₁	255	25	12	292	90	36
L. B ₁	440	21	11	472	88	15
U. B ₂	520	19	8	547	93	11
L. B ₂	505	19	7	531	90	7

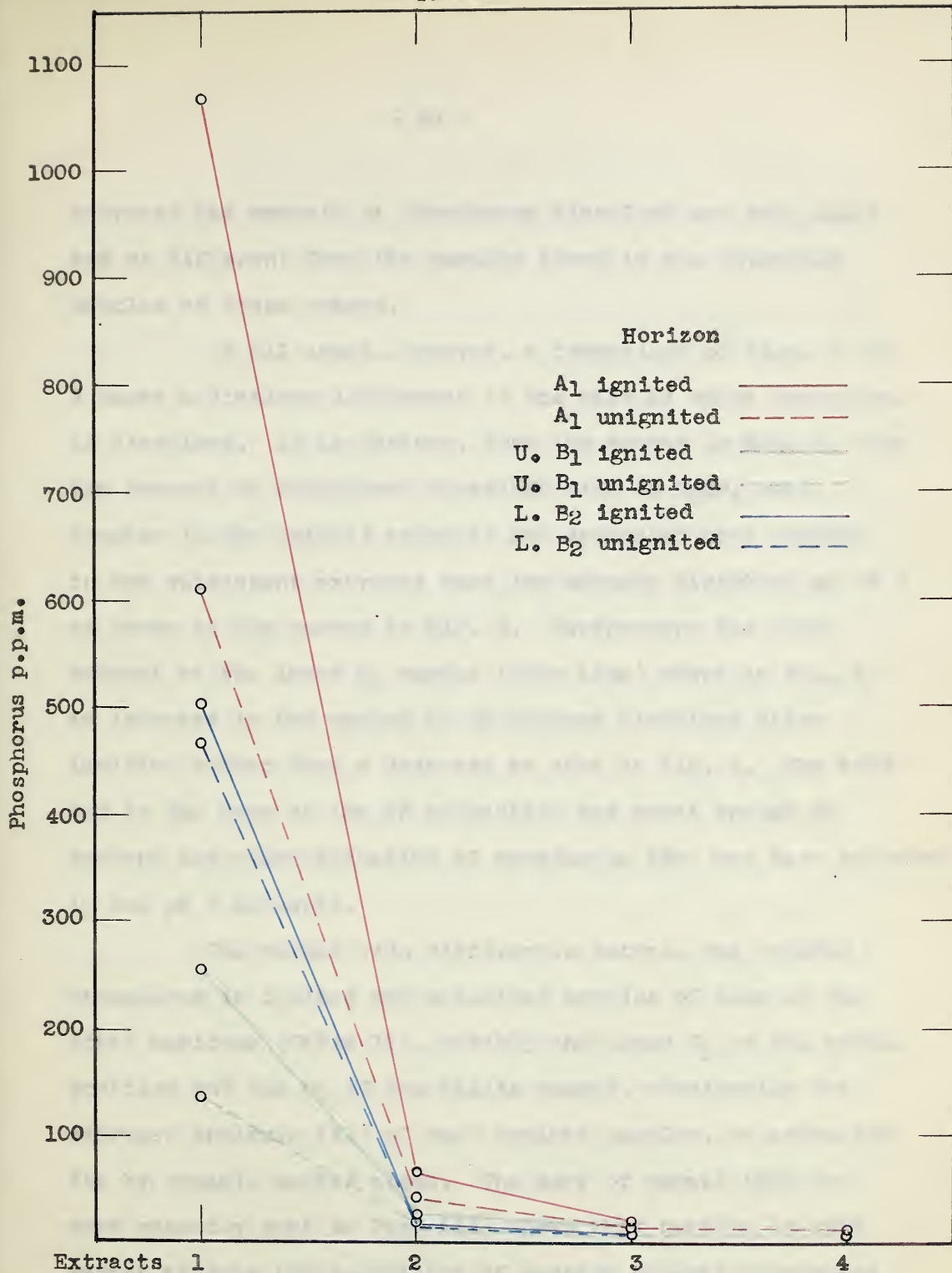
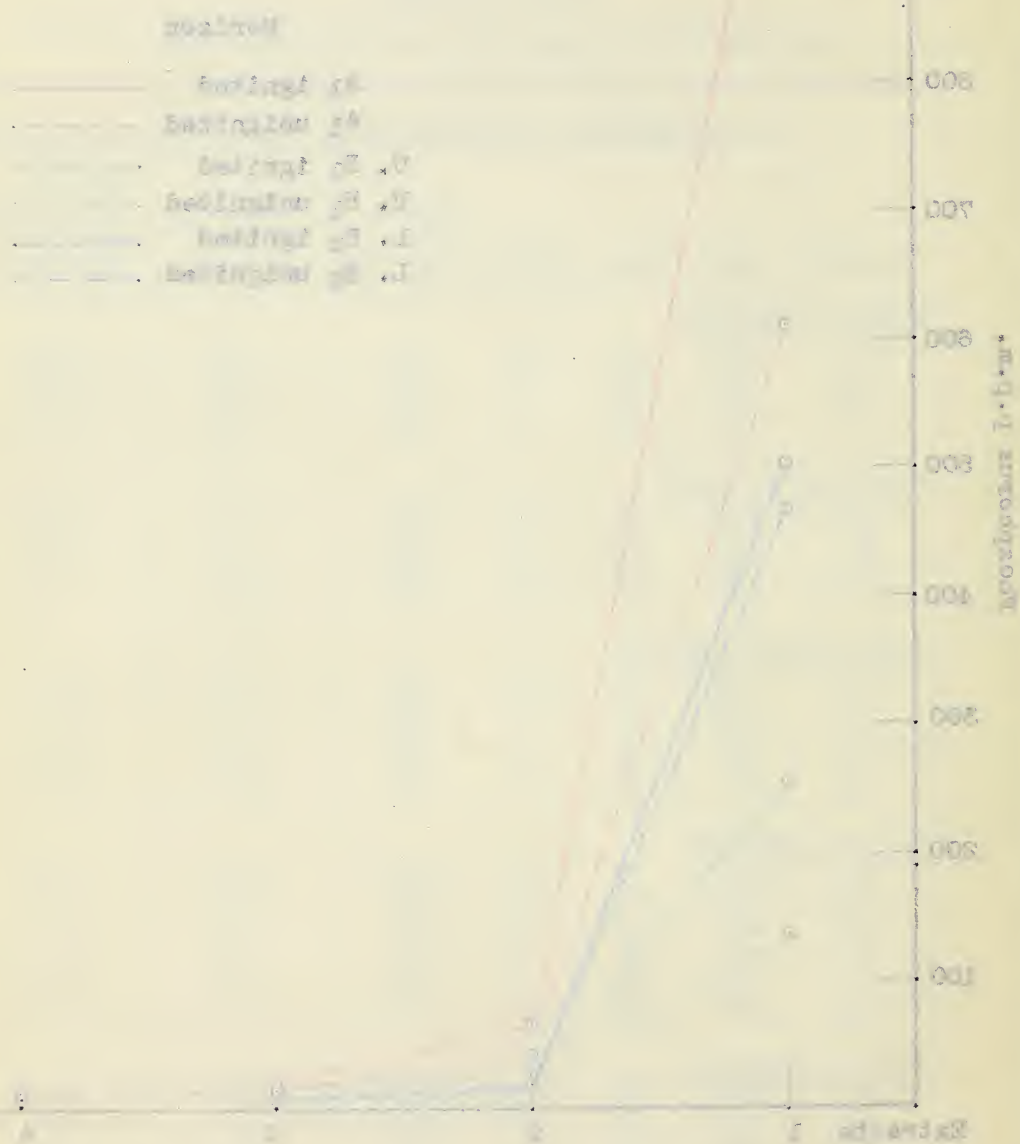


Fig. 3. Breton profile. Soluble phosphorus in 2N H₂SO₄ repeated extracts of ignited and unignited samples of certain horizons.

Fig. 2. Effect of the concentration of the solution of the monomer on the rate of polymerization. The curves are calculated from the experimental data.



extracts the amounts of phosphorus dissolved are very small and no different from the amounts found in the unignited samples at these stages.

In all cases, however, a comparison of Figs. 2 and 3 shows a distinct difference in the rate at which phosphorus is dissolved. It is obvious, from the curves in Fig. 3, that the amounts of phosphorus dissolved with 2N H_2SO_4 were greater in the initial extracts and decreased more rapidly in the subsequent extracts than the amounts dissolved at pH 3 as shown by the curves in Fig. 2. Furthermore the first extract of the lower B_2 sample (blue line) shows in Fig. 3, an increase in the amount of phosphorus dissolved after ignition rather than a decrease as seen in Fig. 2. The acidity in the case of the 2N extraction was great enough to prevent the reprecipitation of phosphorus that may have occurred in the pH 3 extracts.

The rather wide differences between the soluble phosphorus in ignited and unignited samples of some of the other horizons (Table 12), notably the upper B_1 of the wooded profiles and the B_2 of the Fallis cannot, considering the nitrogen analysis (41) of such typical samples, be accounted for by organic matter alone. The work of Marais (23) and more recently that of Ford (11) shows that heating in some manner affects the solubility of certain mineral phosphates.

Bearing this in mind the solubility of iron was investigated in the extracts obtained from ignited and un-ignited soils. The data of Table 13 indicate the possible occurrence of many forms of iron, some increasing in solubility and others decreasing in solubility after ignition. If the iron phosphate occurs as a monohydrate (11) it seems that under the conditions of this experiment it should become dehydrated, liberating its phosphorus and gradually becoming converted to Hematite (Fe_2O_3). In such a case the amount of phosphorus dissolved would be greater while that of iron would be less after igniting, due to this reversion to a less soluble form. Such may be the case in Beaumont B₁ and B₂, the Fallis lower B₁ and B₂, and in most of the Breton.

On the other hand there may be a considerable liberation of iron found in organic combination (29) due to the destruction of organic matter by ignition. The significant increases found in the Provost A₁ and A₂, the Stony Plain A₁ may be due to such causes. In the wooded profiles, however, there is a tendency on podsolization for the iron to be removed from the surface to the subsurface horizons (18) where it may occur rather as some hydrated form.

The observations above are borne out by Marais (23) who, in studying the effect of heating various phosphate minerals at a dull red heat for five hours, concludes that ignition has no effect on the availability of calcium phosphate

Table 13

Soluble iron in 2N H₂SO₄ repeated extracts of ignited
and unignited soils

(expressed as p.p.m. on basis of dry soil)

Horizon	Unignited p.p.m. of Fe in extracts				Ignited p.p.m. of Fe in extracts				Increase Fe due to ignition
	1st.	2nd.	3rd.	Total Fe	1st.	2nd.	3rd.	Total Fe	
Provost (Brown)									
A ₁	1600	480	400	2480	2800	960	720	4480	2000
A ₂	2400	920	840	4160	4000	1080	880	5960	1800
B ₁	2800	1120	720	4640	3400	1120	760	5280	640
C	2600	640	480	3720	3000	920	840	4760	1040
Beaumont (Black)									
A ₁	3200	640	480	4320	3000	1040	620	4760	440
B ₁	2400	720	440	3560	2000	880	640	3520	- 40
B ₂	2800	840	680	4320	2600	800	520	3920	- 400
C	2160	800	600	3560	2600	760	960	4320	760
Stony Plain (Black)									
A ₁	1600	360	240	2200	2000	1040	680	3720	1520
A ₂	1840	400	200	2440	1760	720	640	3120	680
U. B ₁	1360	320	240	1920	1280	640	480	2400	480
L. B ₁	1360	480	320	2160	1440	600	600	2640	480
B ₂	1840	560	440	2840	1760	640	760	3160	320
Fallis (Wooded)									
A ₀	1600	200	120	1920	1520	440	200	2160	240
A ₁	1760	160	120	2040	1440	520	320	2280	240
A ₂	1280	120	80	1480	960	400	280	1640	160
U. B ₁	1440	640	440	2520	2000	640	480	3120	600
L. B ₁	1600	600	560	2760	1200	440	320	1960	- 800
B ₂	1680	680	480	2840	1760	560	400	2720	- 120
Breton (Wooded)									
A ₀	3600	680	240	4520	2800	640	480	3920	- 600
A ₁	5000	720	560	6280	3200	760	560	4520	-1760
A ₂	2200	520	320	3040	1280	520	360	2160	- 880
U. B ₁	2800	880	640	4320	880	720	520	2120	-2200
L. B ₁	2400	880	480	3760	1040	640	480	2160	-1600
U. B ₂	2400	880	600	3880	1600	920	680	3200	- 680
L. B ₂	2400	800	560	3760	2400	880	640	3920	160

but renders the aluminum and iron phosphates remarkably more available. This increased availability of the aluminum and iron phosphates, he points out, may be due to two causes:

(1) Dehydration of the mineral and dehydration of the aluminum and ferric hydrates associated with the phosphate. The dehydrated or partially hydrated oxides resulting, are not as soluble as the fully hydrated ones and would therefore exert less influence on the solubility of the phosphates, their hydrolysis and final assimilation by plants.

(2) Destruction of the physical structure of minerals may greatly alter their solubility. It is pointed out that there are large possibilities for accounting for many riddles with regard to phosphates on the basis of crystalline structure of the minerals, and in this connection the work of Quartaroli showing the possibility of an existence of various isomeric forms of calcium, and possibly iron and aluminum phosphates, is pointed out as a possible solution to some of these riddles. Perhaps the variability of calcium phosphates, aluminum phosphates, and iron phosphates is due to the varying proportions of the different isomers in the several minerals. Ignition may or may not alter the proportions of the various isomers and so exert its effect on the availability of the various phosphates.

Relative Proportions of Easily Soluble, Difficultly Soluble and Organic Phosphorus in Alberta Soils

Considering then some of the wide differences obtained due to ignition, as shown in Table 12, it becomes quite apparent that such differences, as were found for example, in the upper B₁ of the wooded soils, could not be due solely to the liberation of phosphorus held in organic combination but also to some change of the mineral phosphates brought about by ignition.

A determination of the phosphorus held in organic combination cannot be made with great accuracy by the method of ignition, but it is believed that by averaging the resulting increases found in Table 8 and in Table 12 some indication as to the amount of phosphorus held in organic combination would be obtained. However, the increase of phosphorus due to ignition in the pH 3 extraction (Table 8) may serve as a better indication of the amount of phosphorus held in organic combination, especially in the upper horizons, since the increase in iron dissolved was not great enough to account for any great increase in phosphorus. Before ignition it was found that little or no organic matter or iron was dissolved at pH 3 (Tables 4 and 10).

The total phosphorus extracted at pH 3 (Table 7) seems with more certainty to represent the easily soluble phosphorus, the chief form of which is calcium phosphate,

since the amounts of iron and organic matter dissolved were negligible.

The difficultly soluble phosphorus, of which the chief form is the iron phosphate, cannot be determined with certainty from the data presented. However, it seems that some fairly indicative results, as to the amount of phosphorus occurring in difficultly soluble form, may be obtained by difference between the total of the 2N H₂SO₄ extraction (Table 11) and the total of the pH 3 extraction (Table 7) or similar differences after the soils had been ignited (Table 12, Table 8).

The data in Table 14 showing the results obtained by these several methods for the easily soluble and difficultly soluble phosphorus and for the phosphorus held in organic combination reveal a considerable variation in the amounts obtained. The results showing the amount of easily soluble phosphorus (chiefly calcium phosphate) may be taken as fairly indicative of the amount of phosphorus as such occurring in Alberta soils. It will be observed that in all cases (except Breton upper B₁) there is an increase of the easily soluble or calcium phosphate from 25 per cent to 40 per cent in surface horizons to 75 per cent and 80 per cent in the sub-surface horizons. In the case of the Breton upper B₁ the very low proportion of easily soluble phosphorus may be due possibly to one of two factors:

Table 14

Relative proportions of easily soluble, difficultly soluble and organic phosphorus found in representative profiles of Alberta soils
(expressed as per cent of total phosphorus)

Horizon	Total easily soluble phosphorus in pH 3 extracts	Diff. Soluble Phosphorus			Organic Phosphorus			P. insoluble after Igniting and extracting with 2N H ₂ SO ₄
		Total 2N minus total pH 3	Ignited total 2N minus ignited total pH 3	Av.	Ignited total pH 3 minus total pH 3	Ignited total 2N minus total 2N	Av.	
Provost (Brown)								
A ₁	22	12	25	19	45	58	52	8
B ₁	50	11	37	24	8	34	21	5
B ₂	75	4	30	17	-9	17	4	4
C	71	9	30	20	-5	16	6	4
Stony Plain (Black)								
A ₁	38	10	13	12	40	43	42	9
A ₂	41	10	22	11	23	35	29	14
U. E ₁	50	12	22	17	11	21	16	17
L. E ₁	51	13	35	24	-3	19	8	17
B ₂	77	10	23	17	0	13	7	0
Breton (Wooded)								
A ₀	25	9	4	7	69	64	67	2
A ₁	20	32	15	24	52	35	44	13
A ₂	23	29	36	33	32	39	36	9
U. E ₁	18	36	49	43	23	36	30	10
L. E ₁	70	3	22	13	-4	15	6	12
U. E ₂	75	7	14	11	4	11	8	7
L. B ₂	79	4	4	4	7	7	7	10

(1) There may be a concentration in this horizon of very difficultly soluble phosphates due to an accumulation of iron and aluminum colloids. The possible concentration of such colloids in the upper B₁ horizon of the wooded soils has been found by Holowaychuk (17) to be due probably to a precipitation of these colloids brought down in the course of leaching.

(2) The phosphate at first dissolved may have been reprecipitated, as an excess of bases, especially those of iron and aluminum may cause probably considerable precipitation of the phosphate ion even at pH 3 (7,21,30). On the other hand it must be borne in mind that iron and aluminum do not need to enter into solution in order to precipitate phosphate from solution, as colloidal iron and aluminum hydroxides readily combine with phosphorus in solution (32).

The data representative of the difficultly soluble phosphorus vary considerably, the widest difference probably occurring in the Provost profile. Despite this, it seems significant to note that the amounts of difficultly soluble phosphorus as indicated in the unignited column (Table 14) seem fairly constant in the Provost and Stony Plain profiles, except in the heavy lime (B₂) horizon of the Provost. Considering the fact that these soils are alkaline throughout their profiles it seems possible that where such conditions naturally prevail the formation of iron phosphate is inhibited.

Especially does this seem the case where the concentration of lime is greatest (Provost B₂). Such conditions seem most favorable for the formation of calcium or other more easily soluble phosphorus. On the other hand where the soils are more acidic in nature, as in Breton A₁, A₂ and upper B₁ (Table 7) conditions more favorable towards the formation of a high content of iron or difficultly soluble phosphorus prevail, as shown by the fact that 24 to 43 per cent of the total phosphorus in these horizons is difficultly soluble (Table 14, column 2).

Ignition seems to increase the solubility of the difficultly soluble phosphorus, especially in the Provost profile, due possibly to a breaking down of some of the very resistant parent materials, and such increases, where found, may be in part due to these more difficultly soluble forms being dissolved. It would seem then that an average, (Table 14, column 2) of these readings would be more representative of the difficultly soluble phosphorus in these soils.

The relative amounts of organic phosphorus as obtained by the two methods vary considerably. Igniting the soils introduced in the subsurface horizons, at any rate, an appreciable error. Considering the differences obtained on extracting at pH 3 (Table 14, column 3) decreases are seen in many of the horizons while on extracting at 2N appreciable increases are noted in such horizons. The data,

however, seem to agree fairly well for at least the surface horizons, and it is felt that the differences obtained in the two methods will, when averaged, tend to balance each other up to such an extent as to give at least some indication of the proportion of phosphorus held in organic combination in these soils. It is noteworthy that of the total phosphorus found in these soils 42 per cent to 67 per cent exists in organic combination in the surface horizon. From 50 per cent the amount decreases very rapidly to 6 per cent in the C horizon of the Provost, and from 42 per cent in the A₁ of the Stony Plain to about 7 per cent in the B₂ horizon. In the Breton profile the decrease is very gradual in the first four horizons (A₀, A₁, A₂, upper B₁) - from 67 per cent to 30 per cent - while below this the amount drops off to an almost constant average of 7 per cent for the lower three horizons.

Under the most severe conditions of extraction used in this investigation; that is, igniting and then continuously extracting with 2N H₂SO₄, it will be noticed (Table 14, column 4) that in many cases all of the phosphorus was not extracted. The amount remaining represented from 0 per cent to 17 per cent of the total, and it is doubtful if even under more drastic treatment will the total be extracted from some horizons.

Figs. 4, 5 and 6, based on the average amounts of easily soluble, difficultly soluble and organic phosphorus in these three soils, will perhaps serve better to show the relative proportions of these types of phosphorus compounds occurring in Alberta soils.

The data presented in Fig. 4 show that in the surface horizons of the brown soils the phosphorus exists chiefly as organic phosphorus with about equal but smaller proportions of easily soluble and difficultly soluble. In the lower horizons phosphorus occurs chiefly as the easily soluble type with only a small percentage of the organic and difficultly soluble forms.

In the black soils (Fig. 5) the A_1 and A_2 horizons contain phosphorus chiefly in the organic and easily soluble forms with only a very small percentage as difficultly soluble. In the horizons below this the organic phosphorus decreases while the difficultly soluble remains about the same. Both these, however, occur in small amounts as compared to the easily soluble, which seems to be by far the most important form of phosphorus in these horizons.

Similarly the wooded soils (Fig. 6) have in their thin A_0 horizons the largest proportion of the total phosphorus in organic combination, a considerable amount as easily soluble and only a relatively small amount as difficultly soluble.

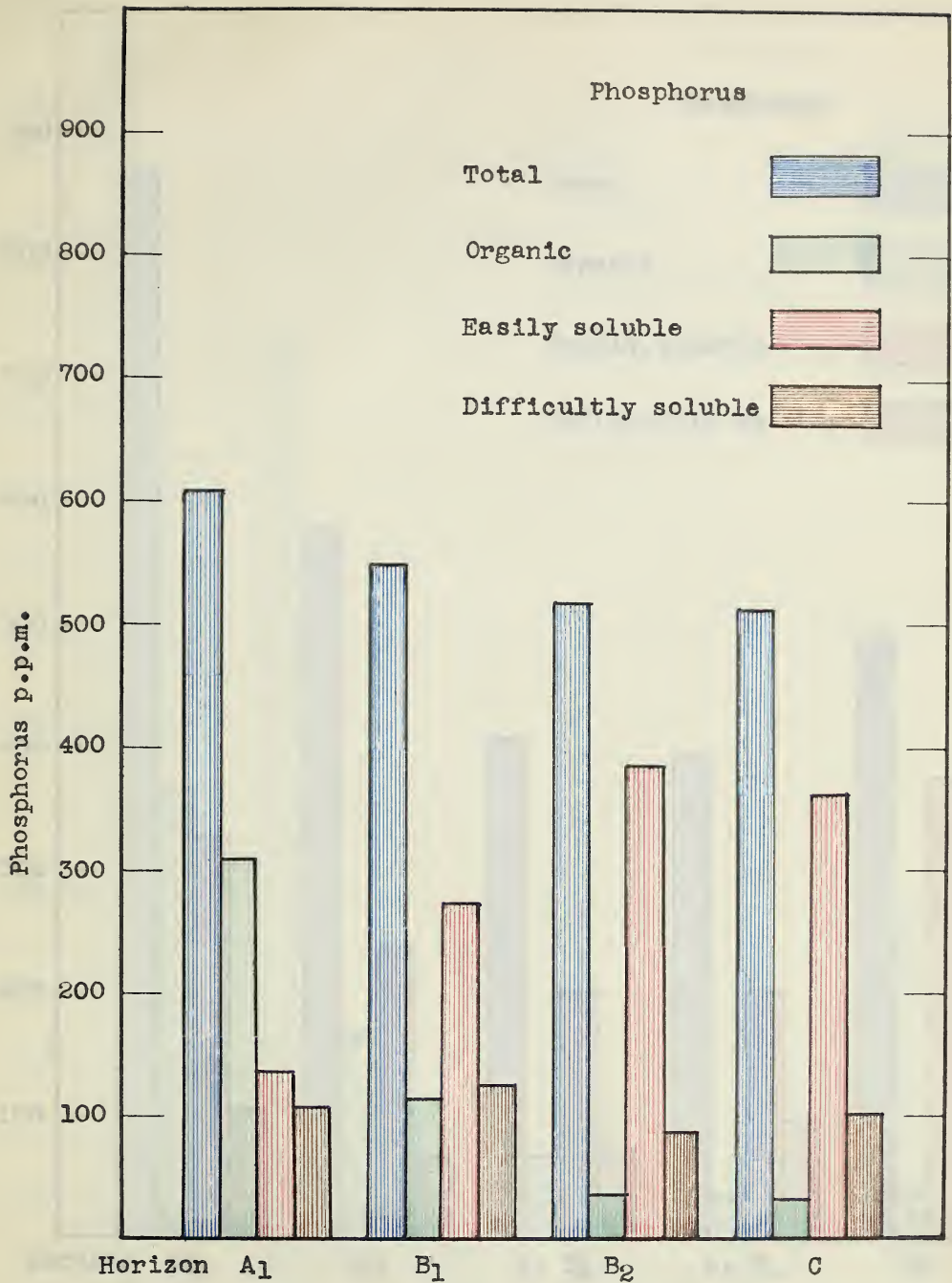
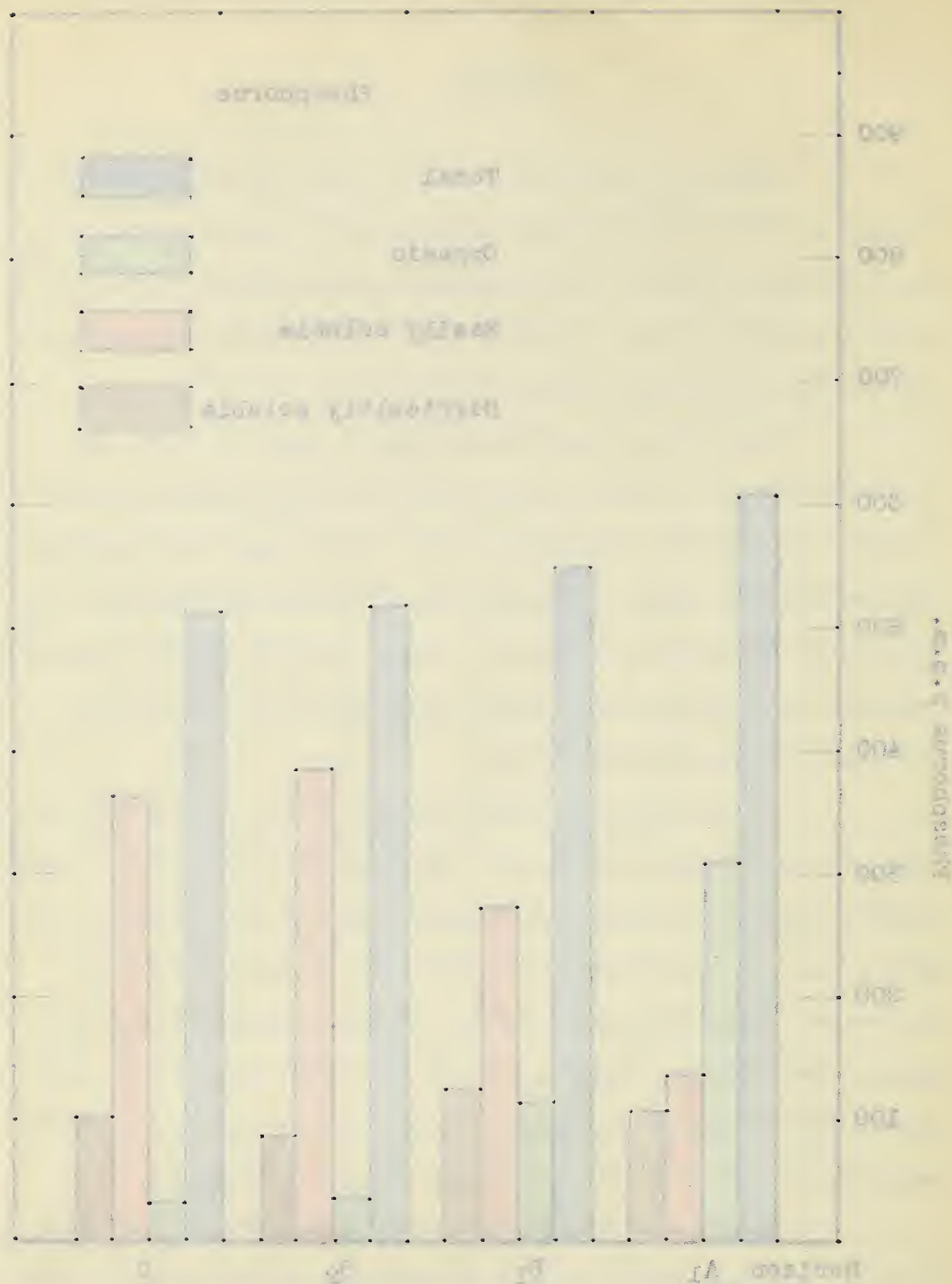


Fig. 4. Provost profile. Relative amounts of total, organic, easily soluble and difficultly soluble phosphorus.

Fig. 4. Proportions of relative amounts of total, organic, easily soluble and diffusible relative phosphorus.



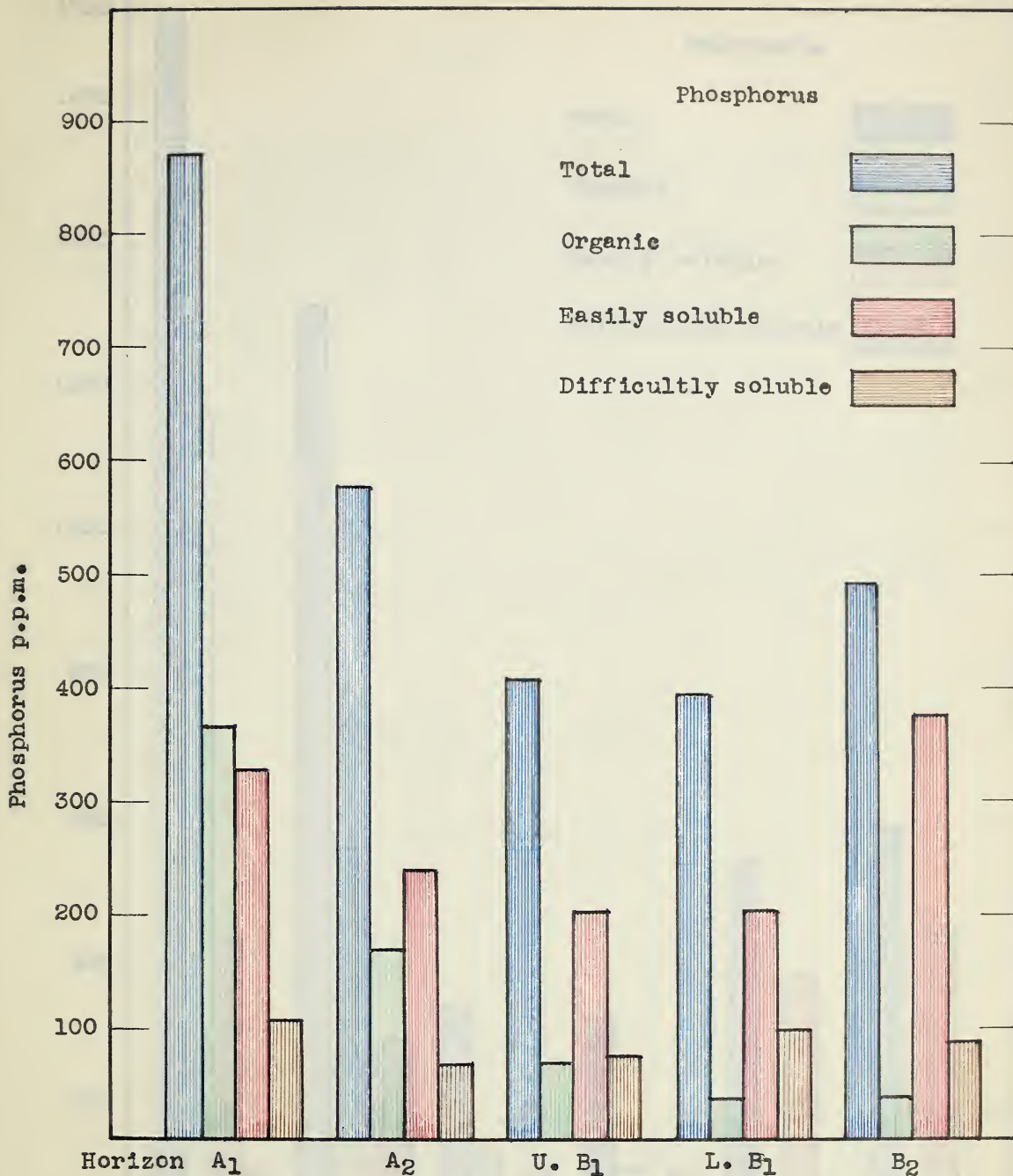
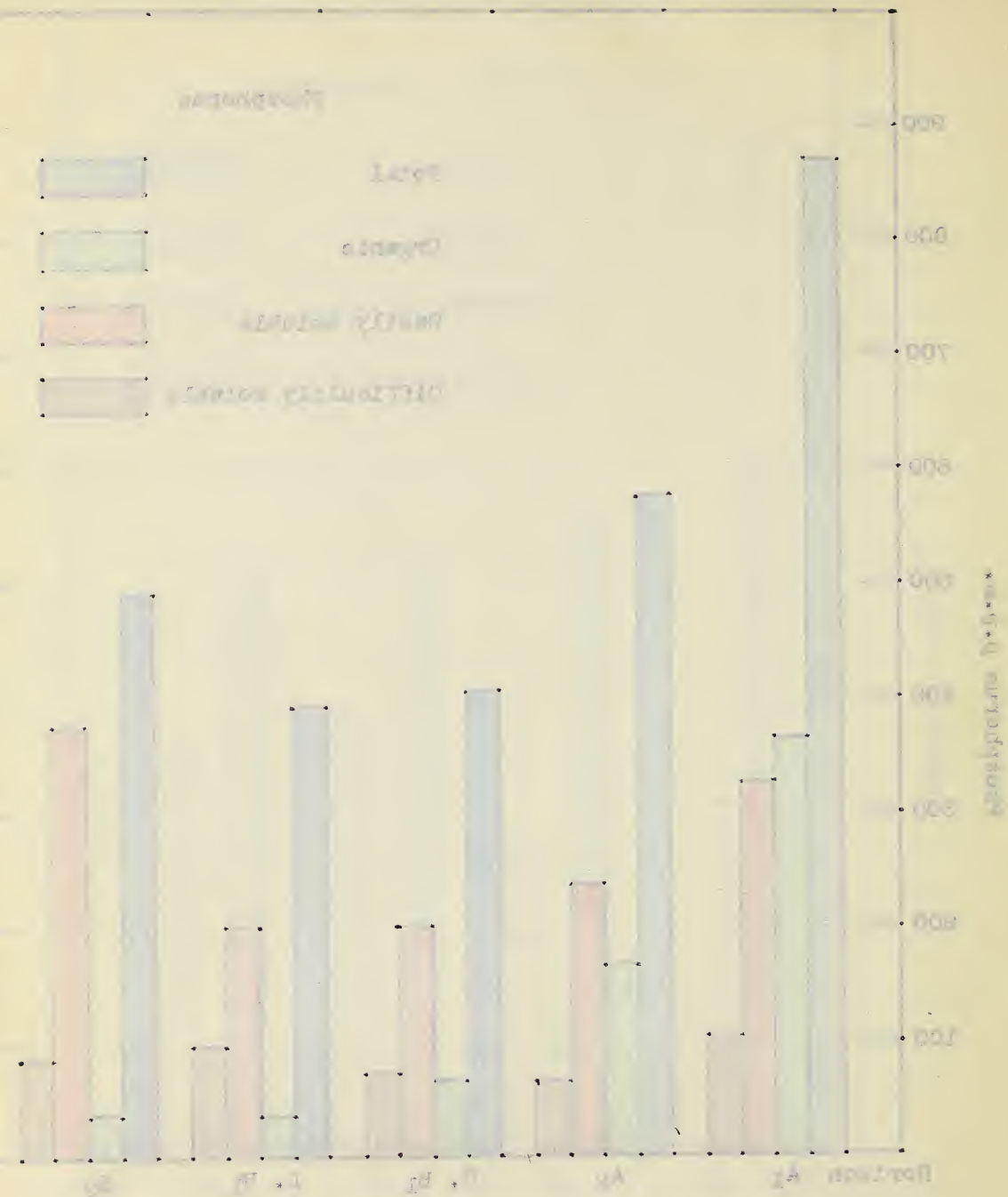


Fig. 5. Stony Plain profile. Relative amounts of total, organic, easily soluble and difficultly soluble phosphorus.

Fig. 2. Body fluid profiles. Left - amount of total, organic, easily volatile and clinically volatile substances.



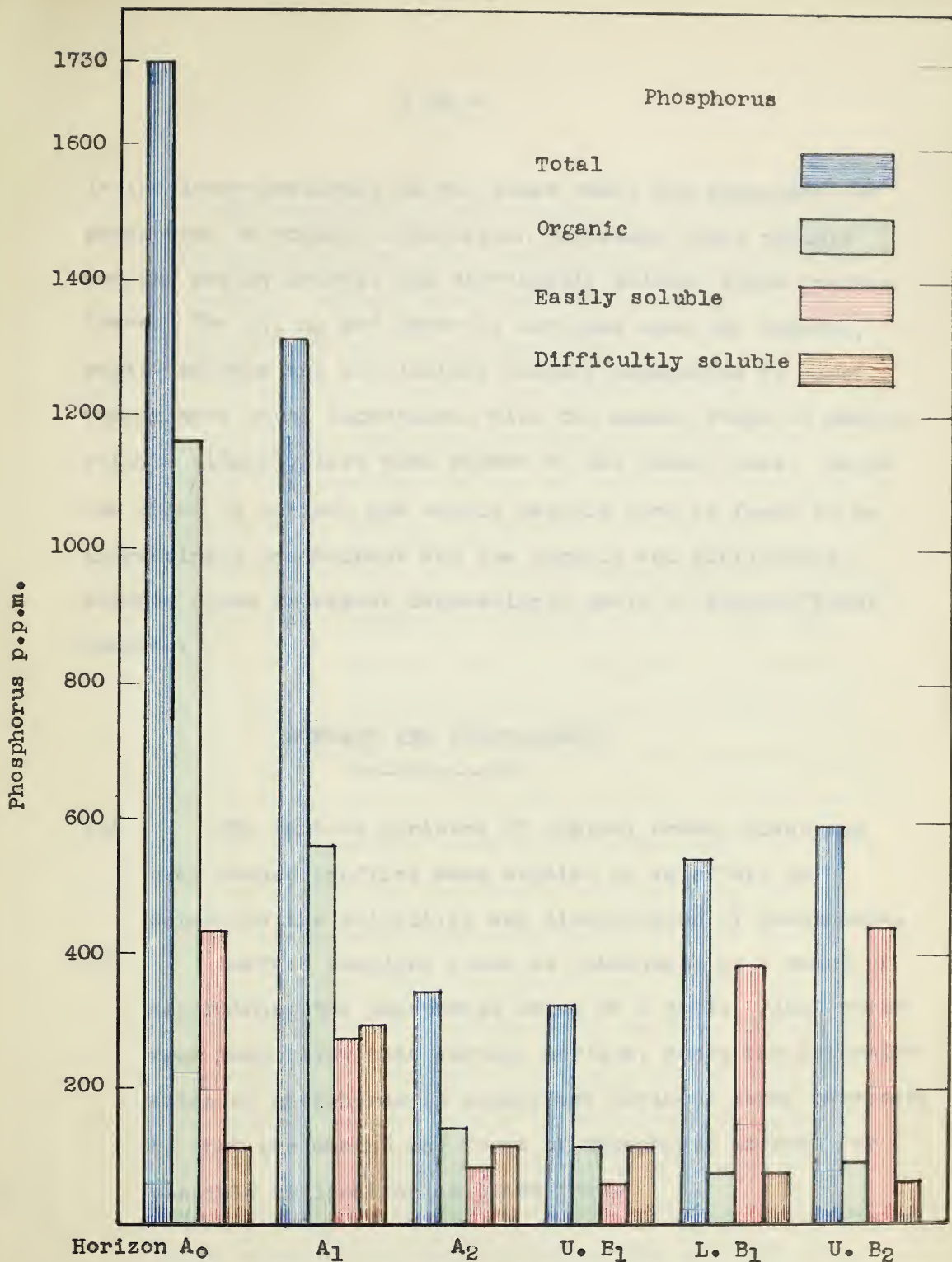


Fig. 6. Breton profile. Relative amounts of total, organic, easily soluble and difficultly soluble phosphorus.

(lower B₂ horizon omitted: similar to upper B₂)

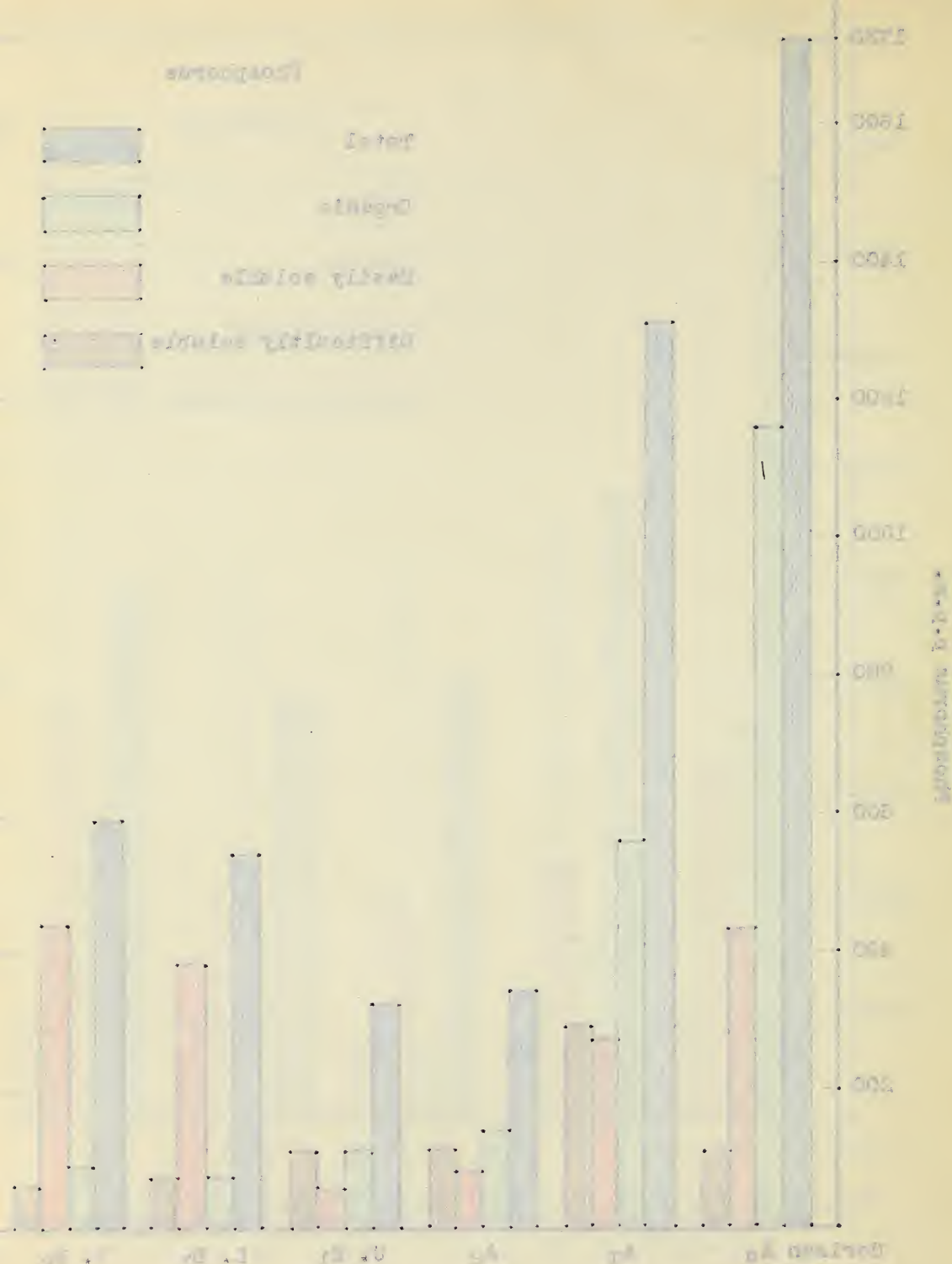


FIG. 3. Relative amounts of total, organic, easily soluble and difficultly soluble phosphorus.

In the lower horizons, on the other hand, the proportion of phosphorus in organic combination decreases quite rapidly and the easily soluble and difficultly soluble forms predominate. The A_1 , A_2 and upper B_1 horizons show the organic, easily soluble and difficultly soluble phosphorus to be of approximate equal importance, with the amount found as easily soluble slightly less than either of the other forms. Below the upper B_1 horizon the easily soluble form is found to be increasingly predominant and the organic and difficultly soluble forms represent decreasingly small to insignificant amounts.

SUMMARY AND CONCLUSIONS

- (1) The various horizons of typical brown, black and gray wooded profiles were studied in an effort to determine the solubility and distribution of phosphorus.
- (2) Surface sampling alone is inadequate as a means of determining the phosphorus value of a soil. Plant roots feed much below this surface horizon, hence the determination of phosphorus in subsurface horizons seems necessary to show the amount and forms of phosphorus present for possible utilization as plant food.

- (3) One extraction alone, especially in the case of weak acid solvents (e.g. .002N H_2SO_4) is insufficient to show the solubility of phosphorus in that solvent. Repeated extractions are necessary.
- (4) In addition to giving a better representation of the soluble phosphorus, repeated extractions tend to show the relative solubility or soil supplying power of phosphorus in various soils and soil horizons.
- (5) In determining the vertical distribution of easily soluble soil phosphorus, extraction at the same pH value in the extracts from all horizons is necessary, for in the case of calcareous B_2 and C horizons, no idea as to the amount of easily soluble phosphorus would have been obtained if they had not been extracted at the same pH value as the A and upper B horizons.
- (6) Easily soluble phosphorus, as determined by repeated extractions with .002N H_2SO_4 buffered to a pH 3, is found to be present in much larger quantities in the B_1 , B_2 and C horizons of the brown profile than in the A_1 horizon. In the black profiles it is present in considerable amounts in the surface horizons, then decreases in the upper B_1 and lower B_1 horizons, but increases to form a large percentage of the total phosphorus in the B_2 or lime horizon. The gray wooded

profiles have a medium amount of easily soluble phosphorus in their A_0 and A_1 horizon, a very small amount in the A_2 and upper B_1 , and then increasingly large amounts in the lower B_1 , upper B_2 and lower B_2 horizons.

- (7) Difficultly soluble phosphorus, as determined by average difference between total extracted with 2N H_2SO_4 and H_2SO_4 at pH 3 from both ignited and unignited samples, is found to be fairly low in all horizons of the brown soil, the parent material included. Only very minor differences, as to the amount of this form, occur between the different horizons. In the black profile, the amount of phosphorus found as difficultly soluble is practically the same in all horizons. The horizons are very low in this type of phosphorus with the A_2 and upper B_1 horizons a little lower than the rest.

The gray wooded profiles show a very small amount of difficultly soluble phosphorus in the A_2 horizon, and a much greater amount in the A_1 , where it occurs in about the same proportion as the easily soluble. Below the A_1 horizon the amount of difficultly soluble decreases gradually, being greater than the easily soluble in the heavily leached A_2 and upper B_1 horizons, but

profiles have a similar amount of easily soluble
phosphorus in their A_1 and A_2 horizons, a very small
amount in the A_3 and upper B_1 , and more than
large amounts in the lower B_1 , upper B_2 and lower B_3
horizons.

(7)

Difficultly soluble phosphorus, as determined by

average difference between total extractable and easily
soluble phosphorus of 25 to 30 from both levels and averaged
profiles, is found to be fairly low in all horizons of
the brown soils, the parent material included. Only very
small differences, as in the amount of total phosphorus,
occur between the different horizons. In the black
soils, the amount of phosphorus found as difficultly
soluble is practically the same in all horizons. The
horizons are very low in this type of phosphorus and
the A_1 and upper B_1 horizons a little more than the
rest.

The grey washed profiles show a very small amount

of difficultly soluble phosphorus in the A_1 horizon,
and a much greater amount in the A_2 , where it occurs
in about the same proportion as the easily soluble.
Below the A_1 horizon the amount of difficultly soluble
phosphorus gradually, being greater than the easily soluble
in the heavily leached A_3 and upper B_1 horizons, but

assuming very insignificant proportions below the upper B_1 horizon. It is noteworthy that the A_1 , A_2 and upper B_1 horizons of the wooded soils were the only ones in this investigation that showed a slightly greater amount of difficultly soluble than of easily soluble phosphorus.

- (8) Organic phosphorus, as determined by difference between the total amounts extracted by the different solvents from soils before and after ignition, occurs in large amounts in the A_0 and A_1 horizons, notably in the gray wooded profiles, but below these surface horizons the quantities of organic phosphorus rapidly diminish approaching insignificant amounts in the B_2 and parent material horizons.

- (9) Ignition of soils at 600°C . for one hour renders a pronounced difference in the amount of phosphorus dissolved by $2\text{N H}_2\text{SO}_4$ or H_2SO_4 at pH 3. In the upper or organic matter horizons there is a large increase due to the destruction of the organic matter. In the lower horizons, however, the differences due to ignition are much smaller. On extracting at pH 3 decreases are found in the B_2 and C horizons of the Provost profile and in the lower B_1 horizons of the Stony Plain and Breton profiles. However, there is a pronounced increase in the horizons of all profiles when extracted by $2\text{N H}_2\text{SO}_4$.

assuming very insignificant proportions below the upper
H horizon. It is noteworthy that the H_1 and upper
H horizon at the second hole were the only ones in
this investigation that showed a slightly greater amount
of diffusible radio in that of easily soluble substances.

(2)

Protein substances, as determined by difference
between the total amounts extracted by the different
solvents from both holes and after ignition, occurred
in fairly constant amounts in the H_1 and H horizons, notably in
the very coated profiles, but rather lower amounts in the
the quantities of organic phosphorus rapidly dissolved
approaching insignificant amounts in the H_1 and upper
H horizons.

(3)

Extraction of radio at 200°C. for one hour showed a
prominent difference in the amount of phosphorus dis-
solved by H_2O , H_2SO_4 or H_2CO_3 at 20°C. In the upper or
organic matter horizon there is a large increase in
on the dissolution of the organic matter. In the lower
horizons, however, the differences are so limited that
only small amounts are extracted at 20°C. horizons and some
in the H_1 and H horizons at the second profile and in
the lower H horizon of the third profile and the pro-
files. However, there is a pronounced increase in the
horizons of all profiles when extracted at 200°C.

These increases seem to be due not only to the destruction of organic matter but also to some change in the solubility of mineral phosphates after ignition.

- (10) Neutralization of extracts with 1-1 ammonia has an intensifying effect on the blue color produced in the test for phosphorus. Since this intensification becomes more pronounced with an increase in the amount of ammonia used, the effect may be due to interfering ammonia salts.

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These impressions seem to be not only to the
impression of organic matter but also to some degree
to the possibility of mineral impurities which
(1) is a description of elements with 1-1 example has
an interesting effect in the sense of the
the last two paragraphs. Since this investigation
remains very prominent with the results of the study
of results here, the effect may be as follows
example 1011.

CONCLUSIONS

The results of the study of the
to Dr. V. A. White. One of the important of 1011,
under which the investigation has been carried
out, and to Dr. A. White for their advice, consultation
and criticism of the manuscript; also to Dr. A. A.
Barnett and others for their co-operation and helpful
suggestions.

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